TECHNICAL REPORT
NATICK/TR-12/020

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INVESTIGATION OF EXPANDABLE POLYMERIC MICROSPHERES FOR PACKAGING APPLICATIONS

by

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June 2012

Final Report
October 2007 – September 2010

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U.S. Army Natick Soldier Research, Development and Engineering Center
Natick, Massachusetts 01760-5018

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
06-06-2012

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
October 2007- September 2010

4. TITLE AND SUBTITLE
INVESTIGATION OF EXPANDABLE POLYMERIC MICROSPHERES FOR PACKAGING APPLICATIONS

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Sarah Schirmer Cheney, Christopher Thellen, and Jo Ann Ratto

5d. PROJECT NUMBER
CFREP TB 08-05

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Natick Soldier Research, Development and Engineering Center
ATTN: RDNS-CFA
Kansas St., Natick, MA 01760-5018

8. PERFORMING ORGANIZATION REPORT NUMBER
NATICK/TR-12/020

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
This report describes a 3-year investigation, ended September 2010, of expandable polymeric microspheres, conducted by the Natick Soldier Research, Development and Engineering Center, to determine the feasibility of compounding microspheres into a polyolefin film to produce a high performance ration packaging material with reduced weight and improved thermal insulation. Polymeric microspheres are small, spherically shaped particles which encapsulate an expandable gas. When the microspheres are heated the gas inside expands, and this increase in free volume results in a decrease in density. Polymeric microspheres are used currently in many applications including; lightweight shoe soles, printing inks, internally pressurized tennis balls, and foaming cable compounds. Microspheres were compounded into high density polyethylene (HDPE) and polypropylene (PP) at various loading levels to successfully produce a polymeric microsphere loaded film for the first time. Three processing trials were completed. The first trial investigated blown and cast monolayer HDPE with powdered microspheres, the second investigated blown multilayer HDPE with powdered microspheres, and the third compared blown and cast monolayer and multilayer HDPE and PP produced usung a microsphere masterbatch. It was determined that multilayer blown film processing utilizing the microsphere masterbatch was the most efficient method of producing a polymer film with reduced density and improved thermal insulation.

15. SUBJECT TERMS
FILMS MATERIALS POLYMER FILMS COST REDUCTION OLEFIN POLYMERS
COSTS PACKAGING MICROSPHERES WASTE DISPOSAL WEIGHT REDUCTION
RATIONS LIGHTWEIGHT BIODEGRADATION MILITARY RATIONS PACKING MATERIALS
SAVINGS POLYOLEFINS WASTE MANAGEMENT THERMAL INSULATION
DENSITY SOLID WASTES ENVIRONMENTAL IMPACT THERMOPLASTIC POLYMERS
POLYMERS BATTLEFIELDS POLYMERIC MICROSPHERES

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
U	U	U	SAR	48

19a. NAME OF RESPONSIBLE PERSON
Sarah Schirmer Cheney

19b. TELEPHONE NUMBER *(include area code)*
508-233-4501

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Preface

This report documents an investigation of the feasibility of incorporating expandable polymeric microspheres into polyolefin films for food packaging applications and the ability of the microsphere-loaded film to reduce the weight of the packaging materials and to improve their thermal insulation, mechanical, and barrier properties. This research was conducted by the Natick Soldier Research, Development and Engineering Center (NSRDEC), from October 2007 to September 2010, as a Combat Feeding Research and Engineering Program (CFREP) technology base project, TB 08-05, *Packaging Materials Incorporating Polymeric Microspheres.*

The effort was lead by personnel from the DoD Combat Feeding Directorate Advanced Materials Engineering Team to include Sarah Schirmer Cheney as the principal investigator (PI), Christopher Thellen who provided Processing Expertise, and Jo Ann Ratto who provided Technical Expertise.

Acknowledgements

The principal investigator (PI) would like to acknowledge the co-authors of this report, Christopher Thellen and Jo Ann Ratto, who provided technical and processing expertise. The PI would like to recognize Danielle Froio who provided processing and permeation expertise. The PI would also like to acknowledge Christopher Hope, Matthew Burke and Gregory Pigeon who completed tensile testing and density analyses. The PI would also like to thank John Song and Corey Hauver for their assistance with thermal conductivity measurements. The PI is appreciative of the CFREP for funding this effort. The PI would also like to thank Francine Frenette of Flint Hills Resources for providing high density polyethylene and polypropylene samples, and Chris Rosenbusch of Akzo Nobel for providing microsphere samples. The PI is also extremely grateful for the guidance and technical support provided by Jeanne Lucciarini, Advanced Materials Engineering Team (AMET) leader.

AN INVESTIGATION OF EXPANDABLE POLYMERIC MICROSPHERES FOR PACKAGING APPLICATIONS

1. Introduction

Polymeric microspheres were investigated by Natick Soldier Research, Development and Engineering Center (NSRDEC) under a Combat Feeding Research and Engineering Program (CFREP) technology base project entitled *Packaging Materials Incorporating Polymeric Microspheres*. This project was funded for three years (FY08-FY10) to focus on applied research. The purpose was to provide information on the incorporation of hollow, expandable polymeric microspheres into thermoplastic polymers to improve the performance of military ration packaging. Objectives included weight reduction of packaging materials, mechanical and barrier property improvement of the packaging materials and introduction of insulating characteristics into the packaging materials to improve the thermal properties.

The US Army has a continuous need to reduce the amount and overall weight of packaging waste generated in the field. Over 34 million Meal, Ready-To-Eat (MRE^{TM}) rations were purchased in 2009, generating over 15,000 tons of waste at an average cost of $50 per ton for collection and disposal [1]. Every MRE^{TM} ration is supplied with a flameless ration heater (FRH), which is packaged in a monolayer high density polyethylene (HDPE) pouch. Any reduction in the packaging waste generated from the use of these heaters would have enormous financial and ecological benefit. The expandable polymeric microsphere is a potential additive that is being investigated for use in ration packaging formulations to decrease the density and thus the weight of a package. An additional benefit of the microspheres is improved insulation to the FRH pouch, thus allowing for faster and more efficient heating.

Polymeric microspheres are small, spherically formed particles with a polyacrylonitrile shell, encapsulating an isopentane gas. When the microspheres are heated, the thermoplastic shell softens, and the internal gas pressure increases, resulting in an expansion of the sphere, similar to a balloon. The diameter of the unexpanded microspheres varies from 10 to 40 µm while the diameter of the expanded microspheres varies from 50-200 µm, with a corresponding decrease in density from 1000 to 3 kg/m^3. Microspheres are commonly used in many applications, including shoe soles (65% microspheres), printing inks (60-80%), and tennis balls and foaming cable filling compounds (over 99%) [2]. According to a literature search, polymer films incorporating microspheres had not been produced prior to this study.

2. Materials, Approach, and Methodology

For this project, microspheres were incorporated into HDPE and polypropylene (PP) in order to demonstrate the feasibility of compounding polymeric microspheres into a polyolefin to produce a thin film. These polymer films were tested in three iterative trials for mechanical properties, oxygen and water vapor barrier, density, optical microscopy, and thermal properties in order to analyze microsphere size and dispersion.

2.1 Materials

Two materials were used in the compounding process: polyolefin resins and polymeric microspheres.

2.1.1 Polyolefin Resins

The two polyolefin resins used in this study were HDPE H3108 and PP 23M2A, both provided by Flint Hills Resources. Both materials conform to FDA regulation 21 CFR 177.1520 (c) 3.2a, which discusses olefin polymers as substances for use as basic components of single and repeated use food contact surfaces [3, 4]. The HDPE is a high moisture barrier material with low gel and a medium molecular weight. The PP is a random copolymer with low extractability and high toughness and impact resistance, as well as autoclave stability. The properties of these materials, including typical barrier properties, are shown in Table 1 [5].

Table 1: HDPE and PP Material Properties

Property	HDPE	PP
Melt Flow Rate (g/10 min)	1.0	2.0
Density (g/cm^3)	0.96	0.90
Oxygen Permeability (cc/m^2)	1550-3100	2325-3100
Water Vapor Permeability (gm/m^2)	4.65-7.75	3.10-7.75

2.1.2 Polymeric Microspheres

Several different microsphere grades, all provided by Akzo Nobel, were investigated including: Expancel 930DU120, Expancel 950DU80, and Expancel 930MB120. Expancel 930DU120 and 950DU80 are dry, unexpanded, powdered microspheres that are compatible with polyolefin resins. The specifications of these microspheres are shown in Table 2 [6]. Expancel 930MB120 is a pelletized masterbatch of 65% 930DU120 microspheres in an ethylene vinyl acetate matrix. This masterbatch grade has a height of foaming of 100-150 mm at 200 °C and a bulk density of 370-450 g/l [7].

Table 2: Dry Unexpanded Microspheres Properties

Expancel Grade	Particle Size (μm)	Expansion Temperature(°C)
930DU120	28-38	191-204
950DU80	18-24	188-200

2.2 Approach

This study consisted of three different processing trials using different combinations of resins and microspheres. In the first trial, HDPE and microspheres were processed into monolayer blown and cast films. The first trial determined that microsphere-loaded polymer films could be produced and what microsphere grade and loading levels would allow for a consistent polymer film formation that would maintain melt stability. In the second trial, multilayer film was processed to allow use of higher microsphere loading levels to improve on the mechanical properties found in the monolayer films while maintaining a smooth surface and melt stability. The third processing trial investigated a wider range of microsphere loading levels and PP as an additional polymer matrix.

2.2.1 First Processing Trial

In the first processing trial, dry unexpanded powdered 930DU120 and 950DU80 microspheres were dry blended, by weight, with powdered HDPE. The HDPE pellets were milled into powder using a Thomas Scientific Variable Speed ED-5 Digital Wiley Mill in order to ensure proper dispersion of the microspheres in the polymer matrix. Both blown and cast monolayer microsphere-loaded films were produced at both high and low temperature profiles. The design of the experiments for the first trial can be seen in Table 3.

Table 3: First Processing Trial Design of Experiments

Sample	Microsphere Loading Level (wt %)	Temperature Profile	Film Types	Film Structure
Control	0	Low & High	Blown & Cast	Monolayer
930DU120	0.50	Low & High	Blown & Cast	Monolayer
	0.75			
	1			
950DU80	0.50	Low & High	Blown & Cast	Monolayer
	0.75			
	1			

Both temperature profiles were investigated in order to determine the optimum extrusion processing temperatures. The barrel and die temperatures for each profile are shown in Table 4. Additional processing conditions and procedures for the first trial can be found in the US Army NSRDEC Laboratory Notebook 10125:27-29 and 10110:70-71.

Table 4: First Processing Trial Temperature Profiles

Temperature Profile	Barrel Temperatures (°C)	Die Temperature (°C)
Low	195, 200, 205, 220	210
High	205, 210, 215, 230	220

2.2.2 Second Processing Trial

Based on the results of the first processing trial, only high temperature profile blown film was produced in the second trial, and only 930DU120 microspheres were added. The loading levels used were 1%, 3%, and 5% by weight. The design of the experiments for the second trial can be seen in Table 5. The barrel and die temperatures used were the same as those used for the high temperature profile in the first trial (shown in Table 4). The processing conditions were identical to the first processing trial. The specific procedures of the second trial can be found in the US Army NSRDEC Laboratory Notebook 10110:72.

Table 5: Second Processing Trial Design of Experiments

Sample	Microsphere Loading Level (wt %)	Temperature Profile	Film Type	Film Structure
Control	0	High*	Blown	Multilayer
930DU120	1%	High*	Blown	Multilayer
	3%			
	5%			

* Barrel temperatures (°C): 205, 210, 215, 230; die temperature: 220 °C

2.2.3 Third Processing Trial

The third processing trial utilized both HDPE and PP with the microsphere masterbatch, 930MB120. Both blown and cast films were produced on both monolayer and multilayer structures in order to quantify the improvement in blown processing compared to cast and the improvement in multilayer compared to monolayer provided through use of the masterbatch. All films were processed using the high temperature profile, with the same barrel and die temperatures used in the first two trials (shown in Table 4). The design of the experiments can be seen in Table 6. The additional processing conditions and procedures used for the third trial can be found in the US Army NSRDEC Laboratory Notebook 10293:29-40.

Table 6: HDPE and PP Design of Experiments

Polymer	Microsphere Loading Level (wt %)	Temperature Profile	Film Type	Film Structure
HDPE	1.62	High*	Blown & Cast	Monolayer & Multilayer
	2.43			
	3.25			
	9.75			
PP	1.62	High*	Blown & Cast	Monolayer & Multilayer
	2.43			
	3.25			
	9.75			

* Barrel temperatures (°C): 205, 210, 215, 230; die temperature: 220 °C

2.3 Methodology

The microsphere-loaded films were processed using the same extrusion equipment in each of the three trials and were analyzed for mechanical properties, oxygen and water vapor barrier, density, microsphere attributes using optical microscopy, and thermal properties during the trials, though not all of the analyses were performed during each trial.

2.3.1 Extrusion

All the films for this study were processed using a Dr Collin GmbH Teach-Line co-extruder (CR72T) with a 20 mm diameter screw and a 25:1 L/D (length/diameter ratio). A 120 mm wide, variable 0.2 to 2.0 mm gap slot die with 20°C chilled rolls was used for the cast film processing (Figure 1). A 30 mm diameter blown film die with a 0.80 mm die gap and a maximum film diameter of 110 mm was utilized for the blown film processing (Figure 2).

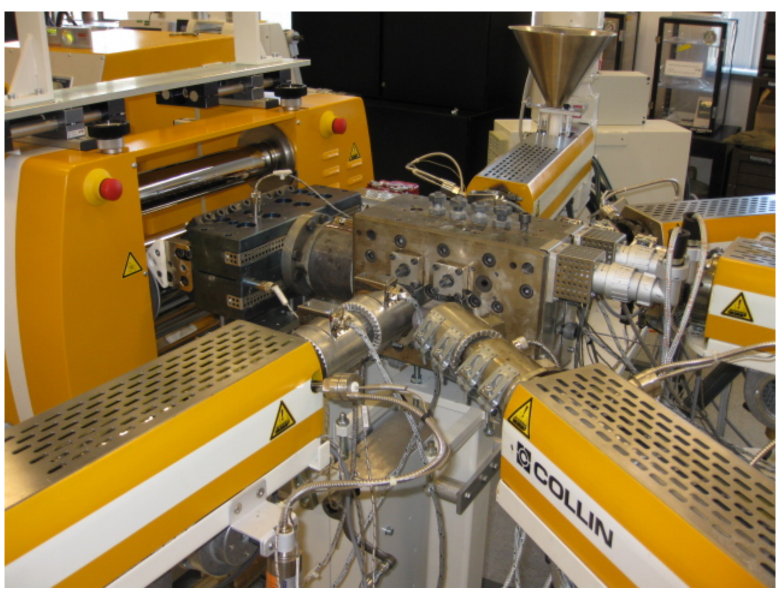


Figure 1: Dr Collin GmbH Cast Film Feedblock and Die

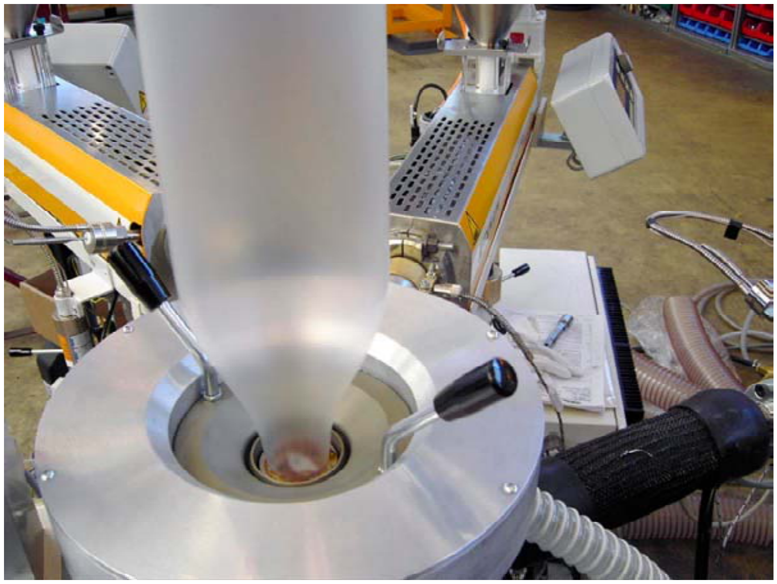


Figure 2: Dr Collin GmbH Blown Film Die

2.3.2 Mechanical Properties

An Instron® 4400R tensile testing machine with a 50 kN load cell was used to determine four tensile properties of the films: Young's modulus, toughness, stress at yield, and strain at break. The specimens were tested at a gauge length of 50.8 mm and a crosshead speed of 50.8 mm/min. For each set of films, 10 specimens were tested following ASTM D882 Standard Test Method for Tensile Properties of Thin Plastic Sheeting. Young's modulus, or modulus of elasticity, is a measure of the stiffness of an elastomeric material and is defined as the ratio of stress over strain. Toughness is the resistance of a material to fracture. Stress at yield, or tensile strength at yield, is the force required to cause permanent deformation of the specimen, i.e., the point at which a material begins to deform plastically, rather than elastically. Strain at break is the ratio of the change in length to the original length of the specimen.

2.3.3 Barrier Properties

The oxygen transmission rate (OTR) was tested using an Illinois Instruments 8001 Permeation Analyzer and a MOCON® Ox-Tran 2/21. For OTR, two 5 cm^2 or 50 cm^2 specimens, depending on the permeation of the sample, were tested at 23°C and 0% relative humidity (RH) following ASTM D3985 Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor. The Illinois Instruments 8001 Permeation Analyzer can test OTR from 0.008 cc/m^2-day to 432,000 cc/m^2-day, and the MOCON® Ox-Tran 2/21 can test from 0.005 cc/m^2-day to 20,000 cc/m^2-day. The OTR of a monolayer film can be normalized by dividing the sample by its thickness, in order to give oxygen permeation rate (OPR) in units of cc-mil/m^2-day.

The water vapor transmission rate (WVTR) was tested using a MOCON® PermaTran 3/31. For WVTR, two 50 cm^2 specimens were tested for each sample at 37.8°C and 90% RH following

ASTM F1249 Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor. The WVTR of a monolayer film can be normalized by dividing the sample by its thickness, in order to give water vapor permeation rate (WVPR) in units of gm-mil/m^2-day.

For monolayer films, OPR and WVPR give a more accurate description of barrier properties because they are measured on a per mil basis; however, permeation rates can only be utilized for monolayer films. Permeation rates are not applicable to multilayer films, as the barrier properties of each layer in the multilayer structure are generally not known. As barrier properties improve, the transmission or permeation rate decreases.

2.3.4 Density Measurement

Five replicates of each sample for density measurement were cut using a 2.54 cm (1 in) diameter circular die. The mass and thickness of each specimen were measured. Thickness was measured in five locations (upper and lower right, upper and lower left, and center), and the measurements were averaged in order to calculate volume. The density was determined by dividing the mass by the calculated volume of the samples.

2.3.5 Optical Microscopy

The microsphere-loaded samples were analyzed for microsphere size and dispersion using a Nikon Eclipse E200 optical microscope with 10X zoom. Q Imaging Micro Publisher 5.0 RTV and Q Capture Pro 6.0 Software were used. An average microsphere size and standard deviation were calculated in order to determine consistency of microsphere dispersion.

2.3.6 Thermal Analysis

Thermal conductivity analysis was completed using a C-Therm TCi Thermal Conductivity Analyzer. Each sample was tested in five locations: upper and lower right, upper and lower left, and center. Ten measurements were taken at each location in order to provide the most accurate thermal conductivity and effusivity data. Thermal conductivity is the property of a material's ability to conduct heat, and thermal effusivity is the square root of the product of a material’s thermal conductivity and heat capacity. Materials exhibiting a low thermal conductivity and low thermal effusivity provide thermal insulation [8].

3. Results

3.1 First Processing Trial

Both the blown and cast monolayer control and microsphere-loaded films processed at both high and low temperature profiles were analyzed for mechanical properties, oxygen and water vapor barrier, and density. In addition, the films were visually inspected for microsphere concentration, flexibility, and surface defects using optical microscopy and were measured for uniformity of thickness using digital micrometers. Thermal analysis was not completed on the monolayer films because the films exhibited a significant surface texture that could have led to significant variations in thermal properties, as contact with the measuring surfaces are critical for thermal conductivity analysis.

During the tests described in the following sections, it was found that better results were produced through use of the high temperature profile rather than the low temperature profile and through addition of the 930DU120 microspheres than the 950DU80 microspheres. Therefore, in some instances during the first trial, those parameters were not tested or the results are not presented in this report.

3.1.1 Mechanical Properties

Four mechanical properties of the films were measured during the first trial: Young's modulus, toughness, stress at yield, and strain at break. Figure 3, Figure 4, Figure 5, and Figure 6 compare Young's modulus values for the control and 930DU120 and 950DU80 microsphere-loaded HDPE films produced at both the high and low temperature profiles. Figure 3 and Figure 4 show the values for the blown films in the machine and transverse directions, respectively. Figure 5 and Figure 6 show the values for the cast films in the machine and transverse directions, respectively. Figure 7, Figure 8, Figure 9, and Figure 10 compare, in the machine direction, the control and 930DU120 microsphere-loaded blown and cast films produced at the high temperature profile for each of the four tensile properties, respectively.

Figure 3 and Figure 4 show that, generally, the high temperature profile produced blown microsphere films with higher Young's modulus values than films produced at the low temperature profile. As can be seen in Figure 3, the 0.75% 930DU120 and 0.75% 950DU80 blown films produced at the high temperature profile had Young's modulus values, in the machine direction, that were 14% and 23%, respectively, higher than those films produced at the low temperature profile. Both Figures 3 and 4 show that, in each direction, five out of the seven films processed at the high temperature profile had higher Young's modulus values than the equivalent blown films processed at the low temperature profile.

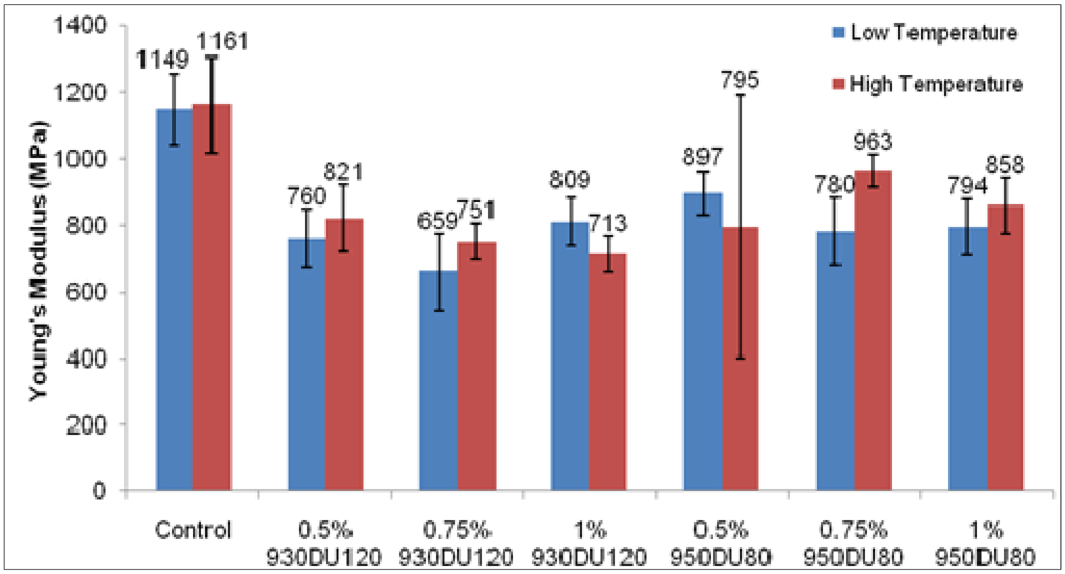


Figure 3: Young's Modulus of Blown Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE, Machine Direction

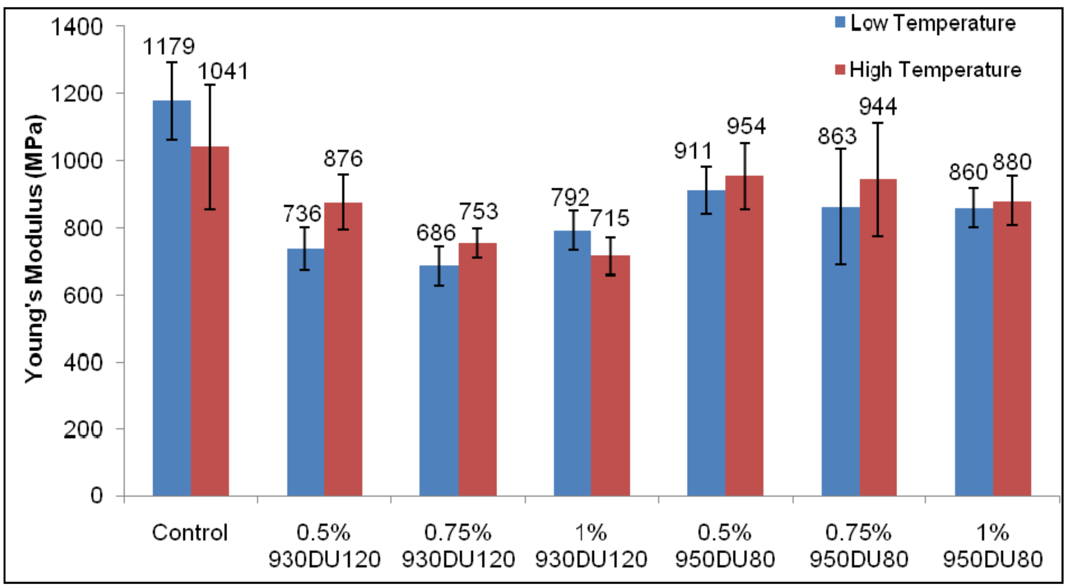


Figure 4: Young's Modulus of Blown Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE, Transverse Direction

However, unlike Figure 3 and Figure 4, Figure 5 and Figure 6 do not show any trends favoring either temperature profile with cast film processing, indicating that processing method significantly affects microsphere expansion and therefore the mechanical properties of the film produced. As can be seen in Figure 5, both the low and high temperature profiles produced microsphere-loaded cast films with Young's modulus values, in the machine direction, that were slightly lower than the controls, which were very similar (760 MPa at the low temperature profile and 754 MPa at the high temperature profile). The 1% 930DU120 cast film had a Young's modulus 14% lower than the control at the low temperature profile and 3% lower at the high

temperature profile. In the transverse direction (Figure 6), the same 1% 930DU120 film had a Young's modulus 5% lower than the control at the low temperature profile and 10% higher than the control at the high temperature profile. As can be seen in Figure 6, the control HDPE cast film, in the transverse direction, had a Young's modulus that was much lower at the high temperature profile than at the low temperature profile, 682 MPa and 793 MPa, respectively. The standard deviation of this film was large, however, indicating inconsistencies in the film.

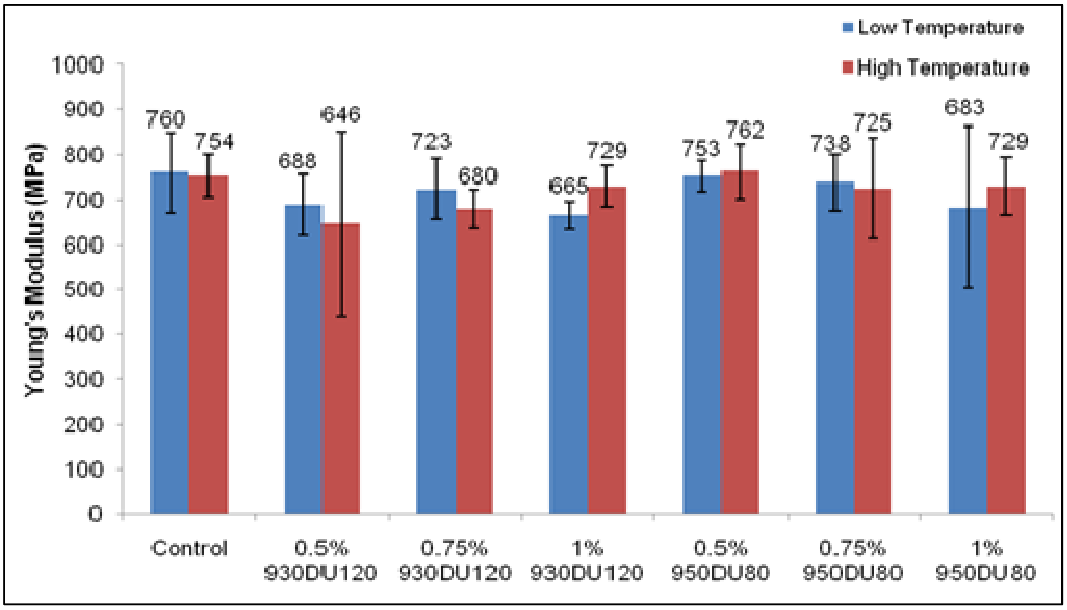


Figure 5: Young's Modulus of Cast Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE, Machine Direction

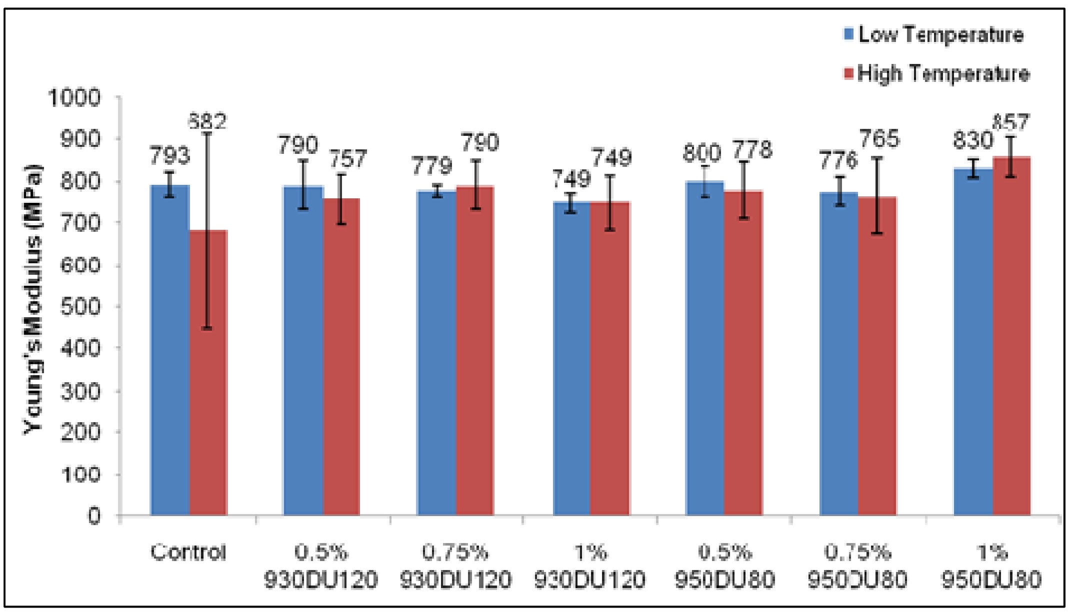


Figure 6: Young's Modulus of Cast Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE, Transverse Direction

In addition, Figure 3 and Figure 4 show that the addition of the microspheres significantly decreased Young's modulus values for the blown film. In contrast, Figures 5 and 6 show much smaller reductions in the values for the cast film and some increases. The microspheres create free volume in the polymer matrix as they expand, thus leading to decreases in mechanical properties such as Young's modulus. Thus, the much higher decreases in Young's modulus in the blown films with the addition of the microspheres indicate much greater microsphere expansion in the blown film than in the cast film. Significant decreases in Young's modulus were found in both directions and at both temperature profiles in the blown films. For example, the 0.5% 930DU120 microsphere-loaded blown film processed at the low temperature profile exhibited a Young's modulus value that was 34% lower than the control in the machine direction (Figure 3) and 37% lower in the transverse direction (Figure 4). The reductions were 29% and 16%, respectively, at the high temperature profile. The reductions in the cast films with the addition of the same 0.5% 930DU120 microspheres were only 9% and <0.5%, respectively, at the low temperature profile and only 14% at the high temperature profile in the machine direction with an increase in the transverse direction.

Furthermore, it can be seen in Figures 3 and 4 that the Young's modulus values for the 950DU80 blown films were generally higher in the transverse direction than in the machine direction; whereas, some of the values for the 30DU120 blown films were higher in transverse direction and others were lower. However, Figures 5 and 6 show that all of the microsphere-loaded cast films had higher Young's modulus values in the transverse direction than in the machine direction.

Figure 7 shows the same data as shown in Figures 3 through 6, but in only one direction (mechanical) with only one grade of microspheres (930DU120) at only one temperature profile (high). This facilitates comparison of the blown and cast processing methods for Young's Modulus. Elimination of some of the parameters in the other Young's Modulus graphs from Figure 7 also facilitates comparison of the two processing methods between Young's Modulus and the other three mechanical properties that were analyzed (shown in Figures 8, 9, and 10, also with the same limited number of parameters). The parameters analyzed but not presented in Figures 7 through 10 were found to be less useful than their counterparts in search of the most viable microsphere-loaded films.

As can be seen when comparing Figure 7, Figure 8, Figure 9, and Figure 10, the blown films were found to have Young's modulus values generally higher than the cast films; however, the blown films were also found to have generally lower values for toughness, stress at yield, and strain at break than the cast films. The blown films showed consistent decreases in Young's modulus, toughness, and stress at yield with increased microsphere loading levels. The strain at break values for the 0.75% and 1% blown films were also lower than the control. However, the value for the 0.50% blown film was actually slightly higher than the control, and the value for the 1% film was actually slightly higher than the 0.75% film. The cast microsphere-loaded films also showed decreases in each of the four mechanical properties as compared to the control films; however, the decreases were inconsistent, possibly due to the high standard deviations that were also observed. In addition, a significant surface texture that could have

led to inconsistencies in mechanical properties was observed in both the blown and cast films. The blown films were found to have more surface texture than the cast films, which could have contributed to lower values for toughness, stress at yield, and strain at break.

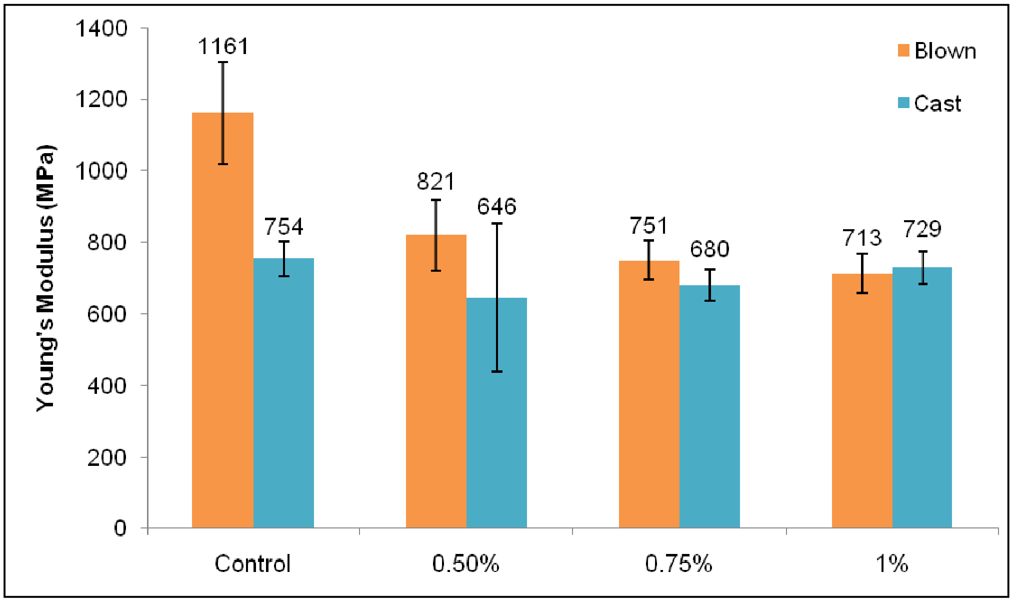


Figure 7: Young's Modulus of Monolayer High Temperature Profile 930DU120 Microsphere-Loaded HDPE, Machine Direction

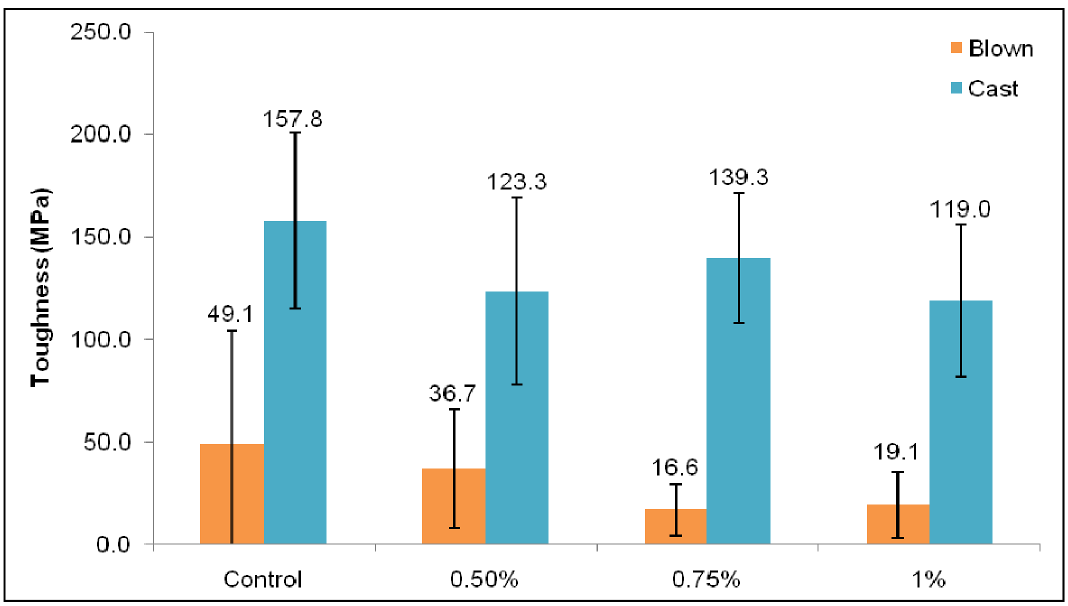


Figure 8: Toughness of Monolayer High Temperature Profile 930DU120 Microsphere-Loaded HDPE, Machine Direction

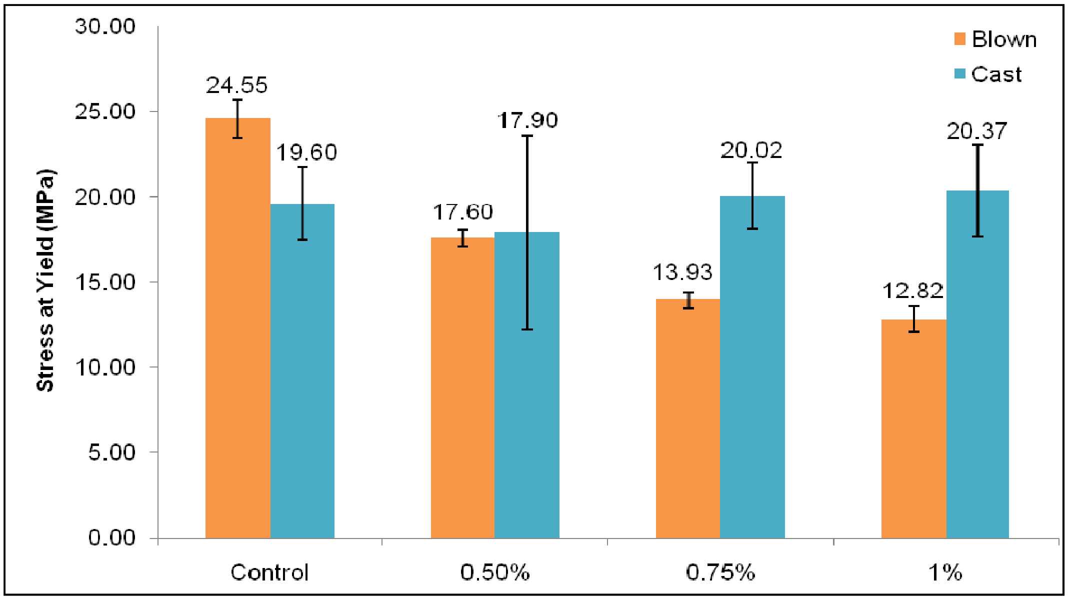


Figure 9: Stress at Yield of Monolayer High Temperature Profile 930DU120 Microsphere-Loaded HDPE, Machine Direction

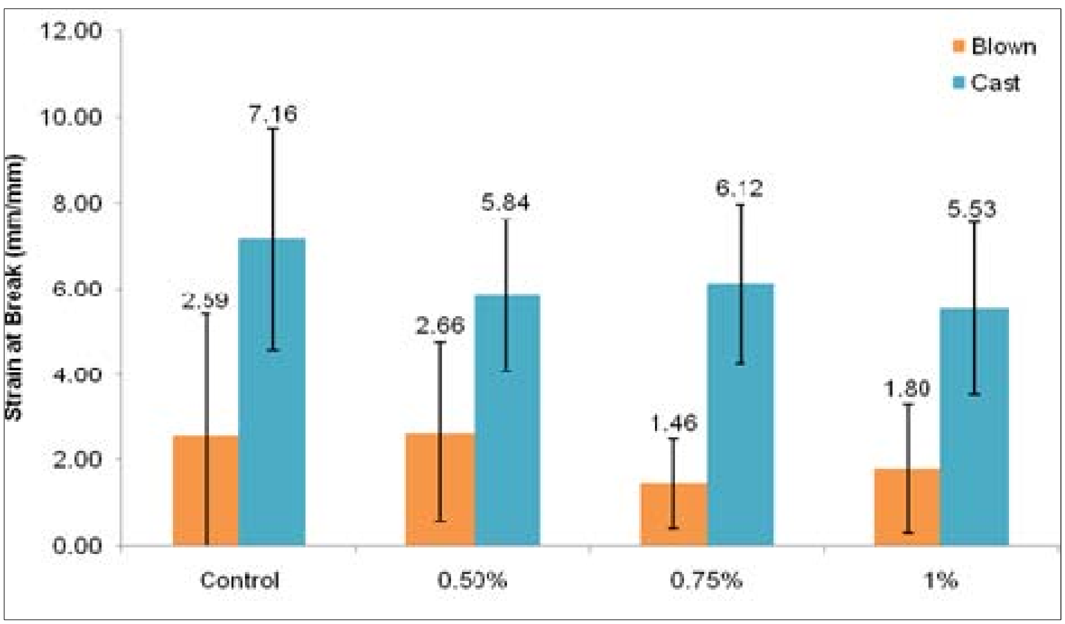


Figure 10: Strain at Break of Monolayer High Temperature Profile 930DU120 Microsphere-Loaded HDPE, Machine Direction

It can be seen in Figure 7 that the Young's modulus of the control HDPE blown film was approximately 50% higher than the control for the cast film. A reduction in Young's modulus was observed in both the blown and cast film systems with the addition of microspheres. However, as mentioned previously, the amount of the reductions was much greater in the blown films than in the cast films. The blown control HDPE had a Young's modulus value of 1161 MPa, which decreased with the addition of microspheres to 821 MPa, 751 MPa, and 713 MPa for 0.50%, 0.75%, and 1%, respectively. The loaded cast values decreased from the control

value of 754 MPa to 646 MPa, 680 MPa, and 729 MPa for the 0.50%, 0.75%, and 1% additions, respectively.

As can be seen in Figures 8, 9, and 10, unlike the Young's modulus values, the values for toughness, stress at yield, and strain at break, respectively, were lower for the blown films than for the cast films, with the exception of the stress at yield values for the controls. The values for toughness and strain at break were substantially lower for the blown films than for the cast films. However, those values were found to have high standard deviations.

3.1.2 Barrier Properties

The OPR and WVPR were measured during the first trial. As discussed previously, the permeation rate is the transmission rate normalized to thickness. Figure 11 and Figure 12 compare OPR at the low and high temperature profiles for the control, 930DU120 and 950DU80 microsphere-loaded HDPE of the blown and cast films, respectively. Figure 13 and Figure 14 compare WVPR for the equivalent films. Figure 15 and Figure 16 compare the OPR and WVPR, respectively, of the blown and cast control and 930DU120 microsphere-loaded HDPE films processed at the high temperature profile that are presented in Figures 11-14. The results from the 950DU80 microspheres and low temperature profile are not included in Figures 15 and 16 in order to facilitate comparison of the blown and cast processing methods. Those parameters were found to be less useful than their counterparts in search of the most viable microsphere-loaded films.

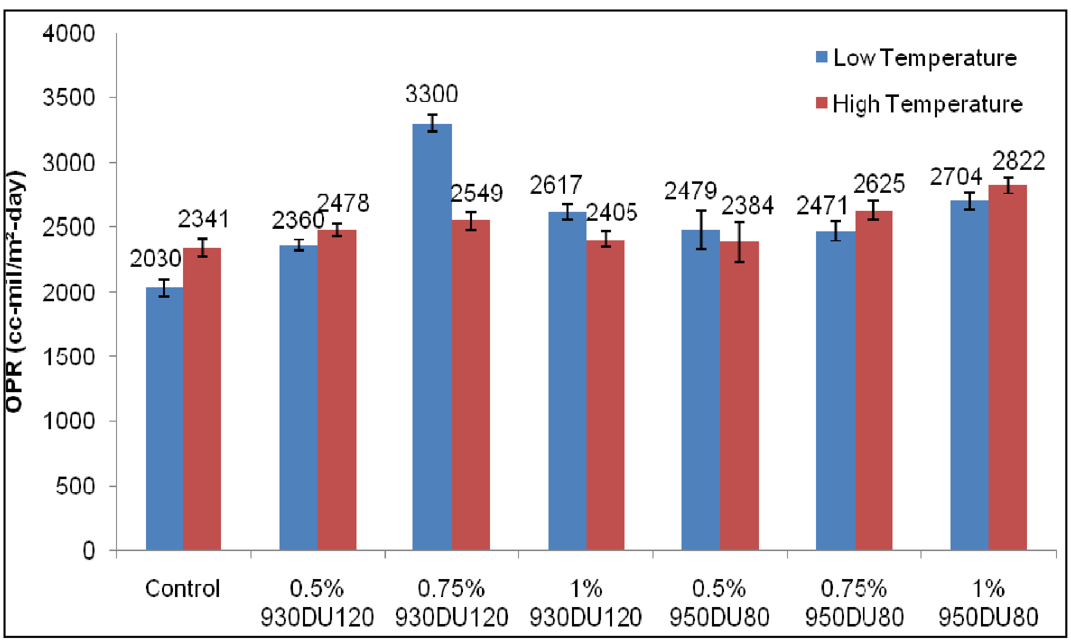


Figure 11: OPR of Blown Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE

Figure 11 shows that, with the exception of the 0.75% 930DU120 low temperature profile sample, the high and low temperature profile blown films had similar OPR, with a slight decrease in oxygen barrier (i.e., higher OPR) with the addition of the microspheres. The blown

control HDPE was found to have a 15% higher OPR when processed at the high temperature profile than at the low temperature profile. However, the OPR of both blown control films (2030 cc-mil/m²-day and 2341 cc-mil/m²-day for the low and high temperature profiles, respectively) were in the same range of oxygen barrier, as HDPE OPR typically ranges from 1550 to 3100 cc-mil/m²-day. No trend favoring the low or high temperature profile was observed with addition of microspheres. Three (0.75% and 1% 930DU120 and 0.5% 950DU80) of the six microsphere-loaded blown films had a higher OPR processed at the low temperature profile than at the high temperature profile while the other three microsphere-loaded blown films had higher OPR at the high temperature profile.

Figure 12 shows that the cast control HDPE had a slightly higher OPR when processed at the low temperature profile than at the high temperature profile, although both values are within standard deviation. Generally, the cast films had a higher OPR when processed at the low temperature profile; thus, the high temperature profile produced a higher oxygen barrier. Only the 0.75% 930DU120 and 1% 950DU80 microsphere-loaded HDPE cast films had higher OPR when processed at the high temperature profile, and the percentage of difference in OPR by temperature profile was greater for the films that had a higher OPR at the low temperature profile. That is, one of the two films (0.75% 930DU120) that had a higher OPR at the high temperature profile had the least difference (0.9% higher) in OPR by temperature profile in Figure 12. The other film with a higher OPR at the high temperature profile (1% 950DU80) had a difference (5.0%) roughly equal to that of the 0.5% 930DU120 film (4.9%) and much less than the 1% 930DU120 film, which had a difference of 7.5%. Generally, the OPR of the cast films remained constant with the addition of the microspheres.

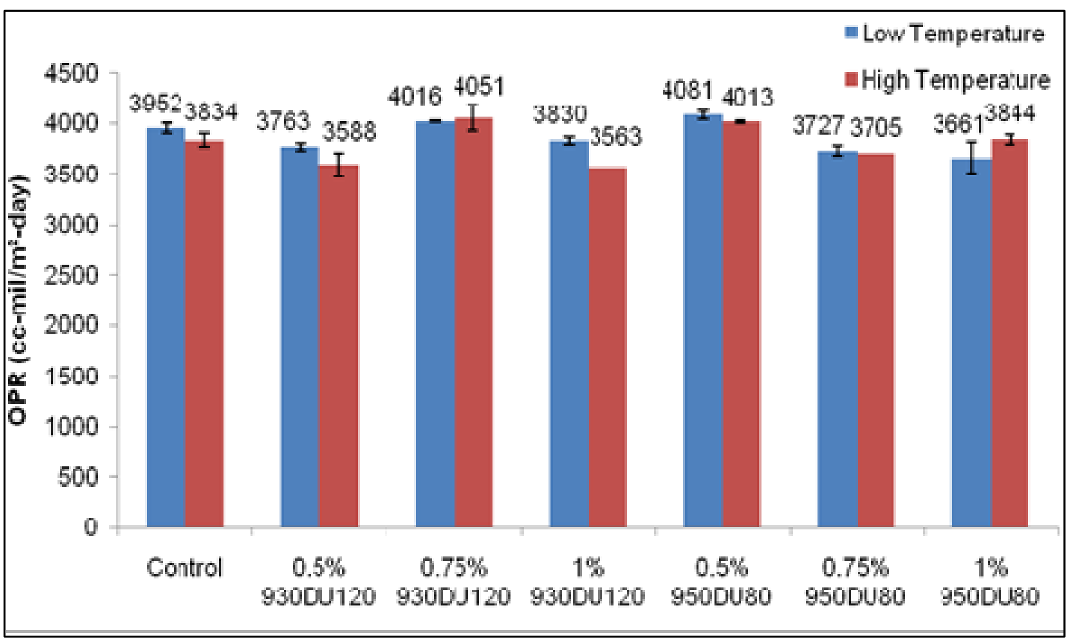


Figure 12: OPR of Cast Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE

Figure 13 and Figure 14 show that the high temperature profile produced slightly lower WVPR than the low temperature profile in both the blown and cast microsphere-loaded films,

indicating that the high temperature profile produced films with a slightly better water vapor barrier. However, the control HDPE films exhibited the opposite effect, with slight increases in water vapor barrier at the low temperature profile. Controls processed at the low temperature profile had a WVPR 13% lower with the blown films and 9% lower with the cast films. In addition, all of the blown films produced much lower WVTR than the corresponding cast samples. Thus the blown films had much better water vapor barrier than the cast films.

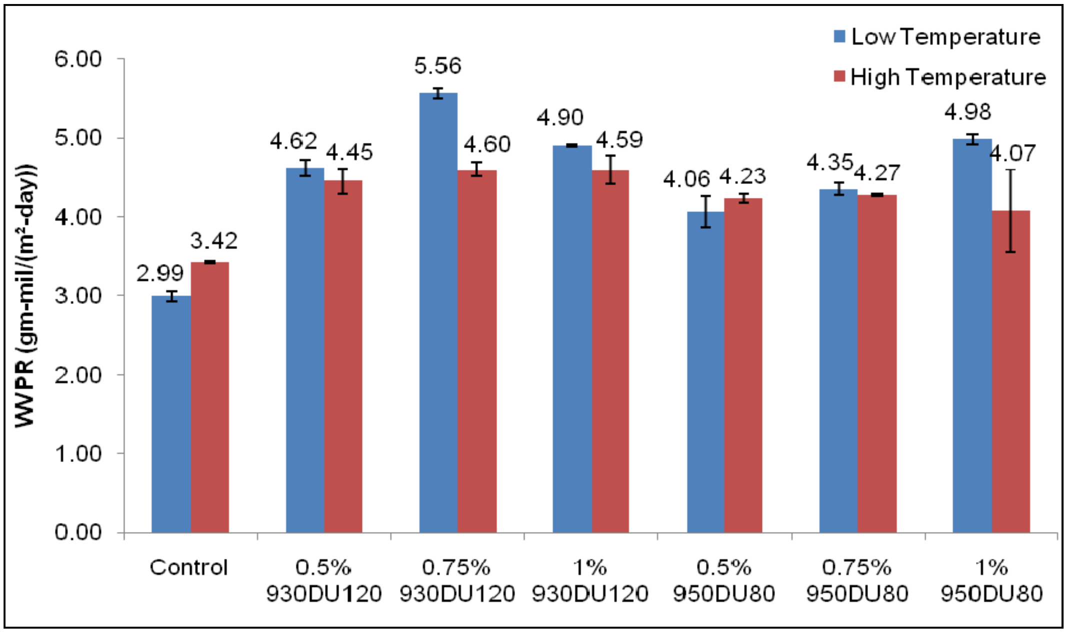


Figure 13: WVPR of Blown Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE

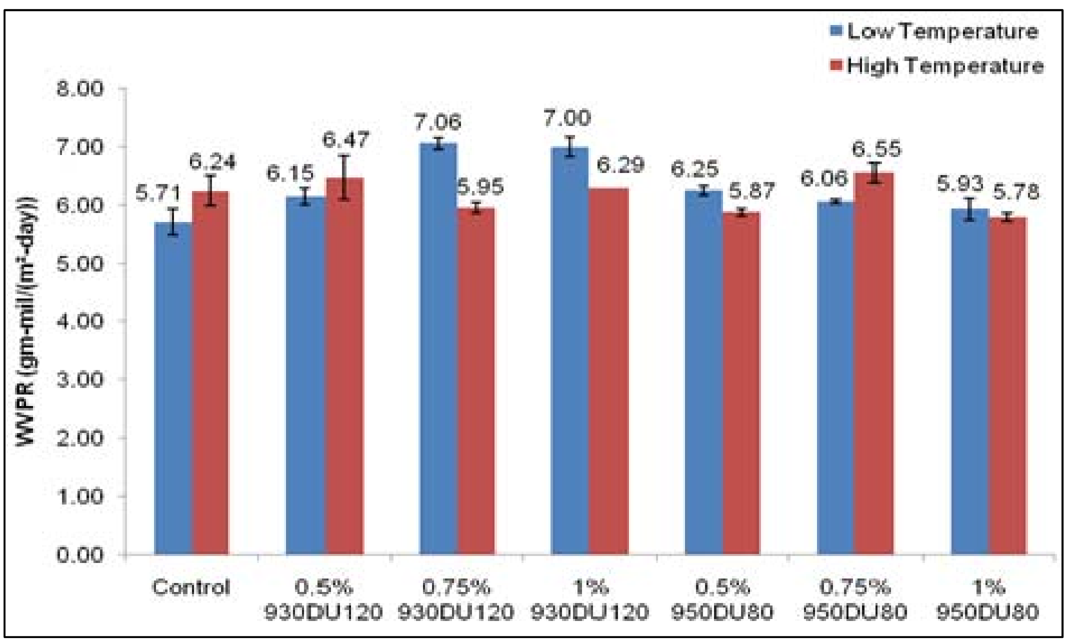


Figure 14: WVPR of Cast Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE

As can be seen in Figure 13, the control for blown HDPE was found to have a WVPR of 2.99 g-mil/m²-day when processed at the low temperature profile and 3.42 gm-mil/m²-day when processed at the high temperature profile. Both of these permeation rates are significantly lower than those typically found in blown HDPE control films, which have ranged from 4.65 to 7.75 gm-mil/m²-day. Thus, both the low and high temperature profile blown controls had significantly improved water vapor barrier properties, as compared to the literature [9]. Although the WVTR for the controls indicate that the low temperature profile produced greater water vapor barrier than the high temperature profile in the control blown films, the microsphere-loaded HDPE blown films showed greater water vapor barrier when processed at the high temperature. For example, the 0.75% 930DU120 HDPE had a WVPR 17% lower when processed at the high temperature profile, and the WVTR for 1% 950DU80 HDPE was 18% lower at the high temperature profile. Figure 13 shows that the addition of the microspheres to the blown HDPE films caused a considerable increase in WVPR, possibly due to the increased free volume introduced by the expanded microspheres.

Figure 14 shows increased WVPR in the cast HDPE films with the addition of the microspheres at all loading levels when processed at the low temperature profile. However, at the high temperature profile, three of the six cast films had lower WVPR than the control with addition of microspheres, and a fourth microsphere-loaded film had only slightly higher WVPR than the control. The WVPR of the cast control at the high temperature profile was 6.24; whereas, the WVPR of the 1% 950DU80, the 0.5% 950DU80, the 0.75% 930DU120, and the 1% 930DU120 were only 5.78, 5.87, 5.95, and 6.29, respectively.

It can be seen in Figure 15 and Figure 16 that the blown films exhibited significantly lower OPR and WVPR than the cast films. These improved barrier properties resulted from the transverse direction orientation induced by the blown film process. In cast film processing the polymer chains are oriented in the machine direction as the polymer flows out of the die. In blown film processing the polymer chains are oriented in both the machine and transverse directions as the polymer flows out of the die and is stretched as the bubble blows up. The blown control HDPE had an OPR of 2341 cc-mil/m²-day, 39% lower than the cast control HDPE, which had an OPR of 3834 cc-mil/m²-day. A slight increase in OPR and WVPR was observed with the addition of the microspheres. For example, the control cast HDPE had a WVPR of 6.24 g-mil/m²-day, and the 0.5% microsphere-loaded cast HDPE had a WVPR of 6.47 g-mil/m²-day. However, generally the permeation rates of both the blown and cast films remained nearly constant with the addition of the microspheres, i.e., no significant reduction in the oxygen and water vapor barrier properties of the resultant films.

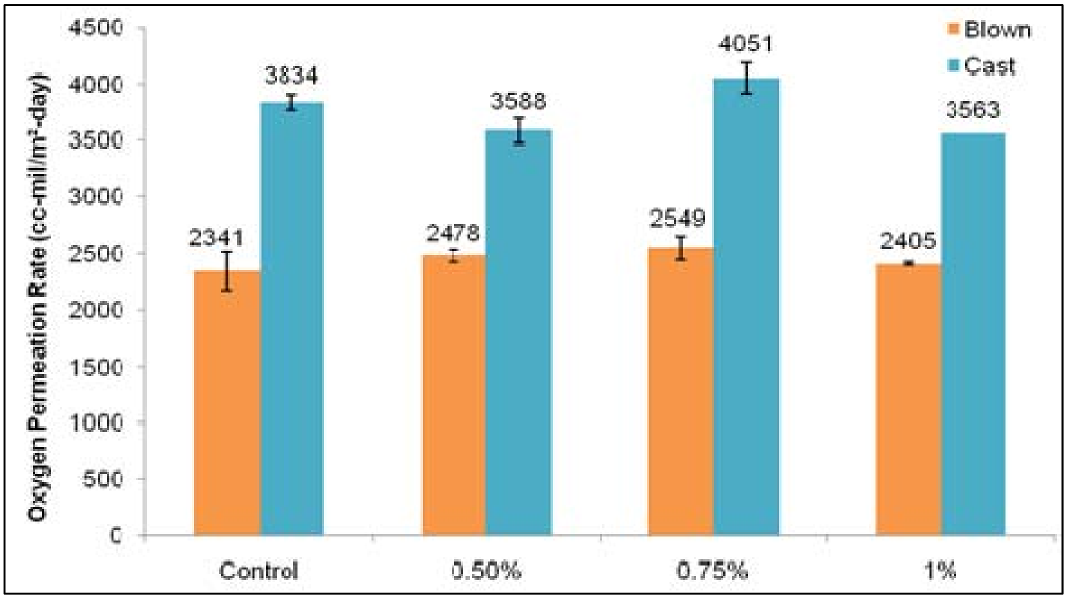


Figure 15: OPR of Monolayer High Temperature Profile 930DU120 Microsphere-Loaded HDPE

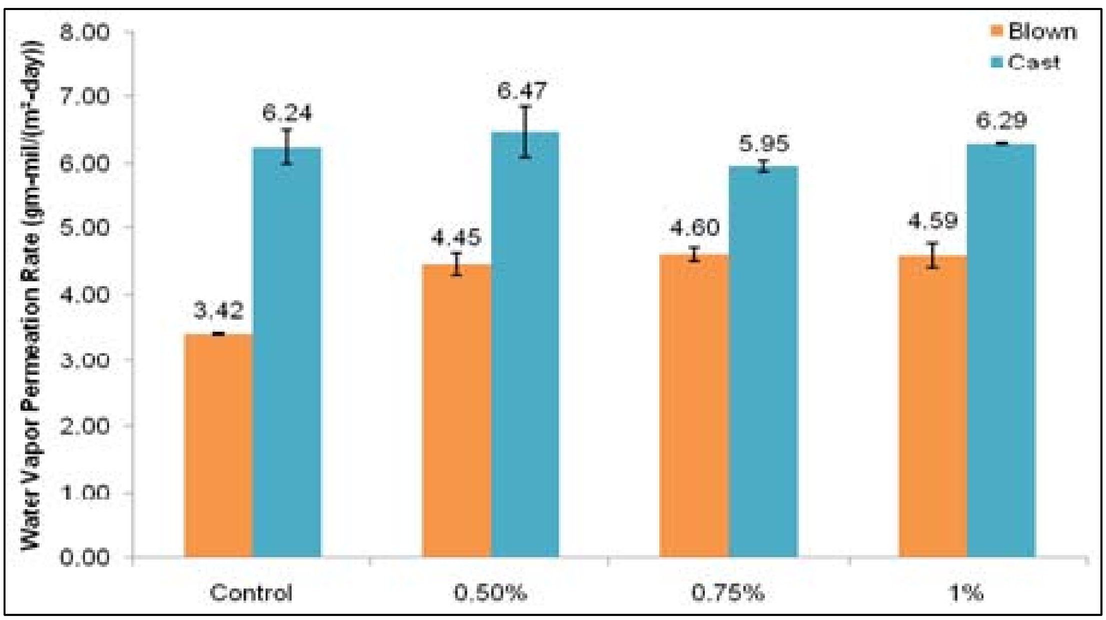


Figure 16: WVPR of Monolayer High Temperature Profile 930DU120 Microsphere-Loaded HDPE

3.1.3 Density Measurement

Figure 17 compares the density at the high and low temperature profiles of the blown control and 930DU120 and 950DU80 microsphere-loaded HDPE films. Only the blown films are shown because no differences between the temperature profiles were seen in the cast microsphere-loaded HDPE films. Figure 18 compares the density of the high temperature profile blown and cast control and 930DU120 and 950DU80 microsphere-loaded HDPE films.

As can be seen in Figure 17, the density of the control HDPE varied slightly, from 0.925 g/cm³ to 0.929 g/cm³, when processed at the high or low temperature profiles, respectively. This minor difference in density can be attributed to experimental error, as both the high and low temperature profile control HDPE densities are within standard deviation. Figure 17 also shows that the addition of the microspheres to HDPE decreased the density of the blown films. In general, the low temperature profile produced blown films with slightly lower densities than the high temperature profile. Only one microsphere-loaded blown film (1% 930DU120, with a density of 0.660 g/cm³ at the low temperature profile and 0.639 g/cm³ at the high temperature profile) had a higher density when processed at the low temperature profile. This general trend indicates increased microsphere expansion at the low temperature profile.

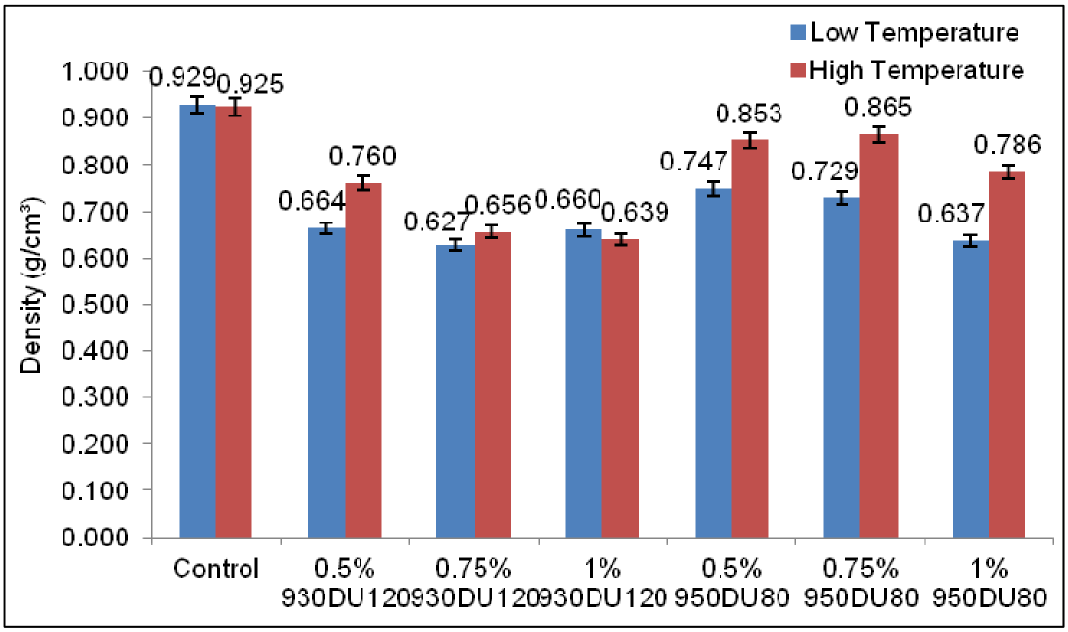


Figure 17: Density of Blown Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE

As can be seen in Figure 18, there was a slight difference in density between the blown and cast control films, likely due to experimental error; however, both density values are within standard deviation. Figure 18 indicates that the blown films had considerably greater microsphere expansion than the cast films. It shows a trend of decreasing density in the blown films with increasing microsphere loading, while the density of the cast films remained similar to the cast control film. In addition, it can be seen that the 930DU120 microsphere grade reduced the density of the blown films by a greater amount than did the 950DU80 microsphere grade blown films at the same loading levels. At 0.5% loading, the density of the 930DU120 film was 12% lower than the density of the 950DU80 film; at 0.75% loading, the density was 32% lower; and at 1% loading, it was 23% lower. This decrease in density shows that the 930DU120 microsphere grade expanded more than the 950DU80 with blown film processing at the high temperature profile. The unexpanded 930DU120 microspheres were slightly larger than the unexpanded 950DU80 microspheres, as shown in Table 2, indicating that the expanded 930DU120 microspheres would also be slightly larger.

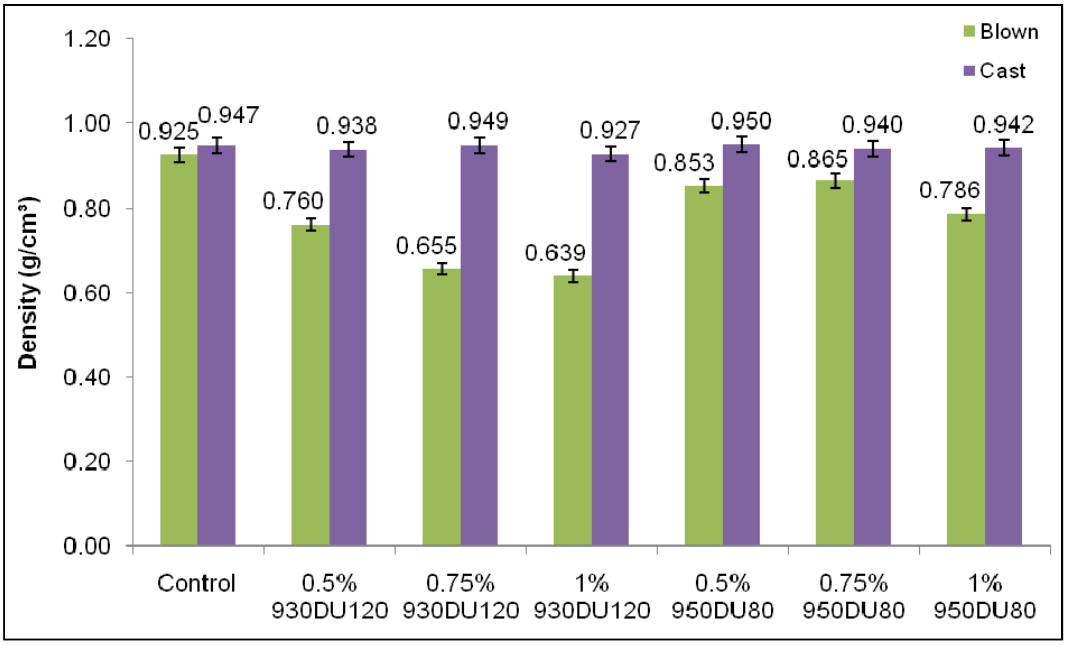


Figure 18: Density of High Temperature Profile Monolayer 930DU120 and 950DU80 Microsphere-Loaded HDPE

3.1.4 Optical Microscopy

Figure 19 and Figure 20 show optical microscopy images comparing the blown and cast 1% 930DU120 microsphere-loaded films produced at the high temperature profile. The blown 1% microsphere-loaded film was found to have a greater visible concentration of microspheres and greater microsphere expansion than the cast 1% microsphere-loaded film. The optical microscopy images show that the blown microspheres expanded from approximately 33 µm to approximately 110 µm, while the cast 1% microspheres expanded from approximately 33 µm to only approximately 85 µm. Therefore, blown film extrusion was found to be preferable to cast film extrusion. Blown film processing provides the microspheres with additional time before solidification of the polymer melt after exiting the die, thus allowing the microspheres to continue expanding as the film is slowly cooled. Cast film processing, on the other hand, solidifies the polymer melt immediately upon contact with chilled rolls, significantly reducing microsphere expansion.

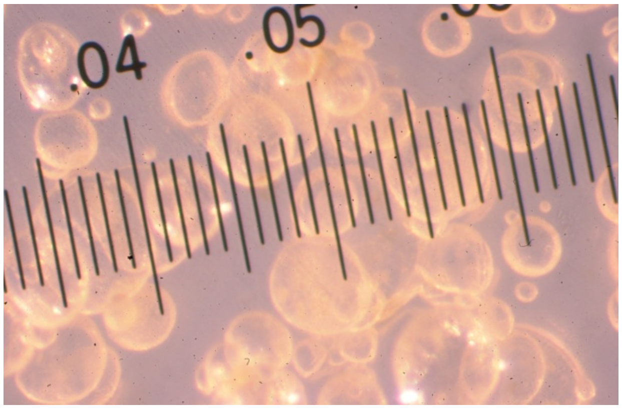


Figure 19: Optical Microscopy Image of Blown Monolayer 1% 930DU120 Microsphere-Loaded HDPE

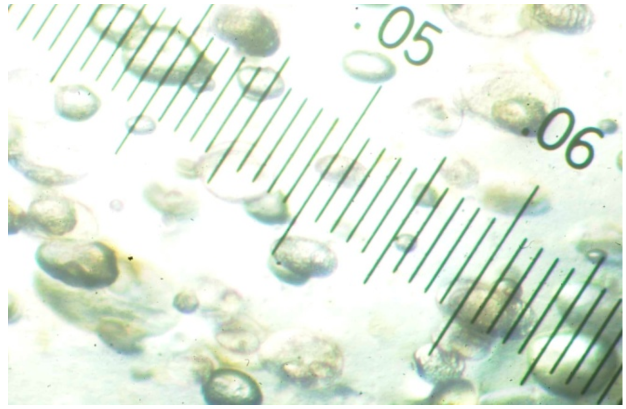


Figure 20: Optical Microscopy Image of Cast Monolayer 1% 930DU120 Microsphere-Loaded HDPE

3.1.5 Discussion of First Trial Results

The first trial determined that blown film processing using the high temperature profile along with 930DU120 microspheres provided a film with the greatest microsphere expansion and barrier properties. These films did exhibit a significant surface texture, however, which could have led to a decrease in mechanical properties in the monolayer film. It was expected that multilayer blown film processing would allow for the production of higher loading level films with smooth surface textures and improved mechanical properties.

Although the blown films were found to have slightly decreased tensile properties, the microsphere dispersion and barrier properties were significantly greater than those of the cast films. The blown film processing produced a more uniformly dispersed microsphere film than the cast film process. The blown films also had a more uniform thickness, as measured by digital micrometers, and greater overall dispersion of the microspheres, as determined by visual inspection of optical microscopy images. The cast film process produced films with an uneven microsphere dispersion, which had a greater concentration of microspheres towards the center of the film. Although the density measurements (Figure 17) indicated that the films at the low temperature profile had greater microsphere expansion, it was also found that the films produced at the high temperature profile were more flexible and had a greater and more uniform microsphere concentration, fewer surface defects, and greater tensile and barrier properties than the films produced at the low temperature profile.

3.2 Second Processing Trial

Because of the desirable microsphere expansion and barrier properties found in the blown film using the high temperature profile loaded with 930DU120 microspheres and the limitations found with the monolayer film during the first trial, multilayer HDPE film was used in the second trial and was only processed using blown film extrusion at the high temperature profile, and only the 930DU120 microspheres were added. Higher loading levels (1%, 3%, and

5%) were used to determine whether multilayer film would maintain melt strength and produce a smooth surface with increased microsphere loading. The films were analyzed for mechanical properties, oxygen and water vapor barrier, density, and thermal properties, but optical microscopy was not performed due to time and schedule constraints. The results obtained during the first trial for the blown, high temperature profile monolayer control and 930DU120 microsphere-loaded films were compared to results found during this trial.

3.2.1 Mechanical Properties

Figure 21, Figure 22, Figure 23 and Figure 24 compare, in the machine direction, the monolayer and multilayer control and 930DU120 microsphere-loaded high temperature profile blown films for four tensile properties: Young's modulus, toughness, stress at yield, and strain at break, respectively. Only machine direction data are shown because similar trends were observed in the transverse direction. In general, the monolayer and multilayer films exhibited a decrease in tensile properties with increasing microsphere loading level.

As can be seen in Figure 21, the monolayer control was found to have a Young's modulus approximately 10% higher than the multilayer control, but both films were within standard deviation. Both the monolayer and multilayer microsphere-loaded films showed lower Young's modulus values than the control films. The monolayer microsphere-loaded films decreased in Young's modulus from 821 MPa at 0.5% to 751 MPa at 0.75% and 713 MPa at 1% loading. Similarly, the multilayer microsphere-loaded films decreased in Young's modulus from 517 MPa at 1% to 510 MPa at 3% and 493 MPa at 5%. Interestingly, Figure 21 illustrates that at 1% the monolayer film had a higher (38%) Young's modulus than the multilayer film.

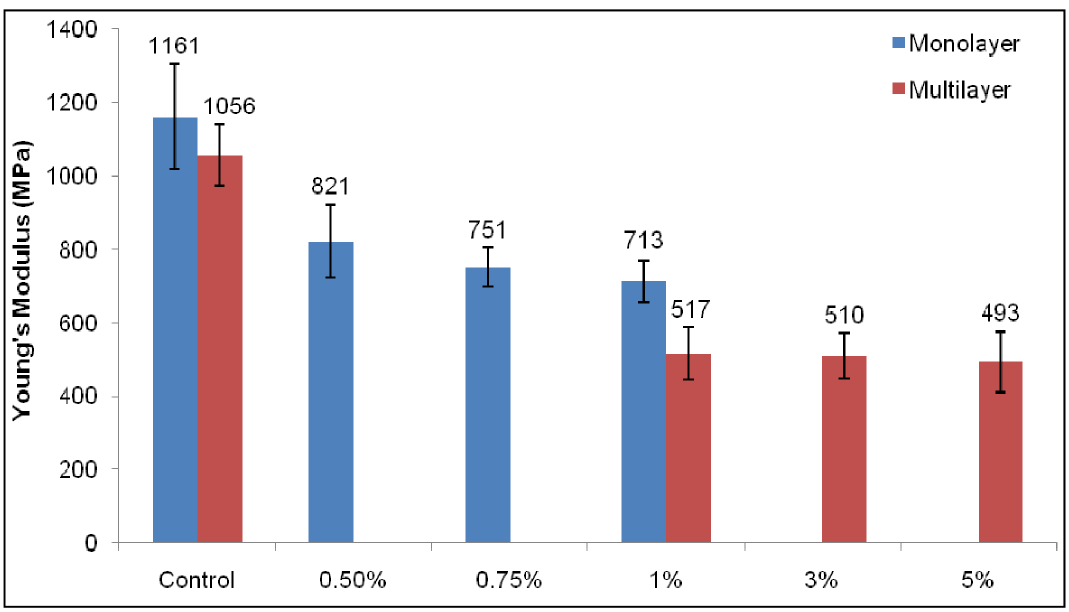


Figure 21: Young's Modulus of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE, Machine Direction

As expected, the multilayer films had higher values for the other three tensile properties, as shown in Figure 22, Figure 23, and Figure 24. The 1% multilayer film had a toughness more than double the monolayer film, stress at yield was 37% higher, and strain at break was 80% higher. This trend can also be seen (in Figure 21, Figure 22, and Figure 23) with the control films. The multilayer control had a higher toughness, stress at yield, and strain at break than the monolayer control, although, as with Young's modulus, both films were within standard deviation for each of these measures.

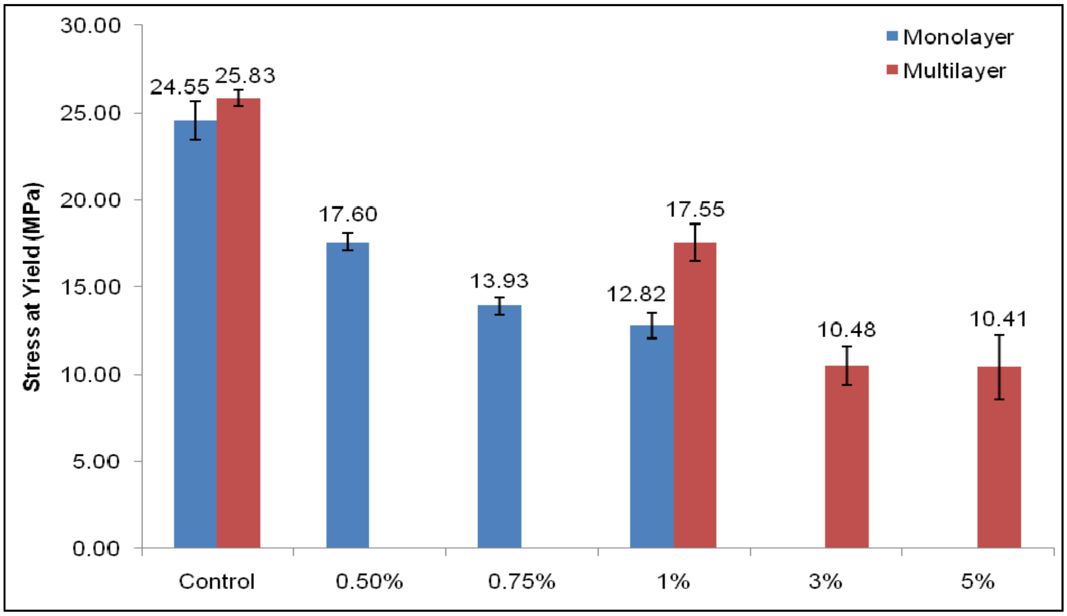


Figure 22: Stress at Yield of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE, Machine Direction

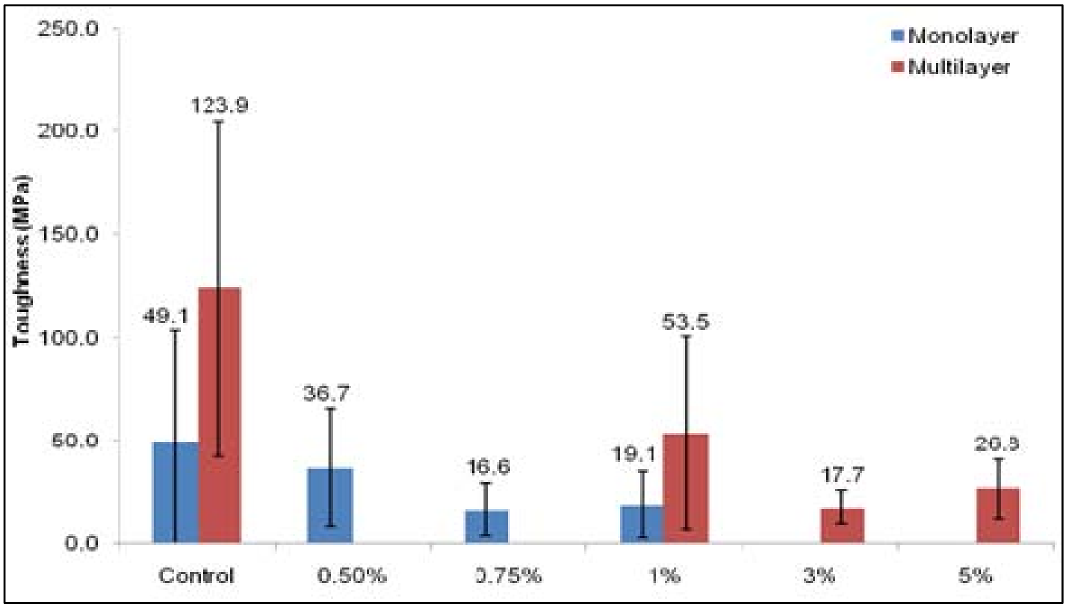


Figure 23: Toughness of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE, Machine Direction

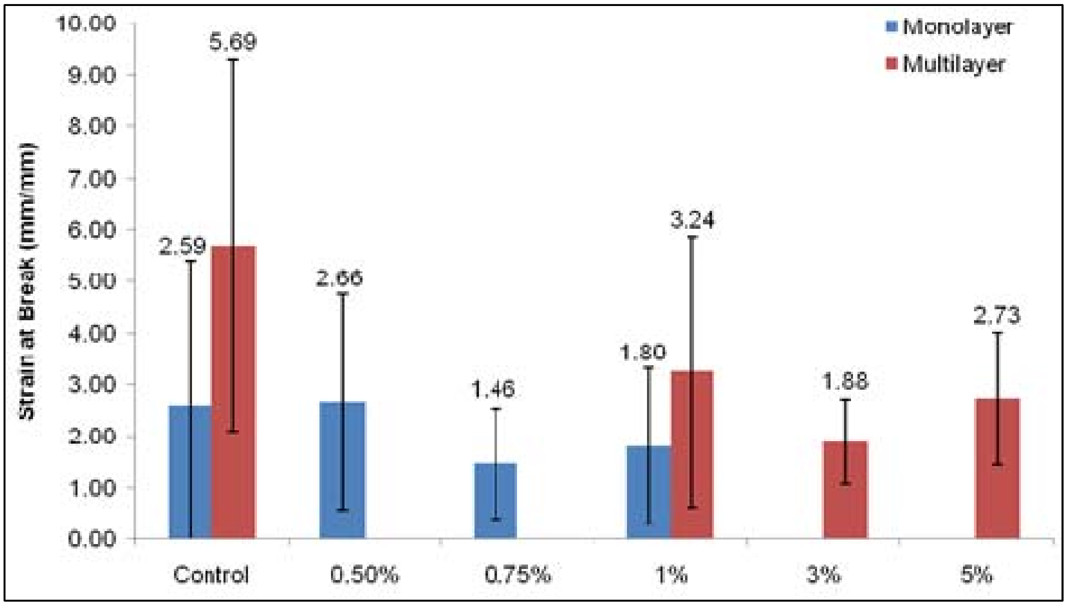


Figure 24: Strain at Break of High Temperature Profile Monolayer and Multilayer Blown 930DU120 Microsphere-Loaded HDPE, Machine Direction

3.2.2 Barrier Properties

Oxygen and water vapor transmission were measured during the second trial, with oxygen and water vapor permeation provided for comparison of films with varying thickness. Figure 25 and Figure 26 compare the oxygen barrier properties of the control and 930DU120 microsphere-loaded HDPE monolayer and multilayer high temperature profile blown films. Figure 25 compares the OTR while Figure 26 compares the OPR. Figures 27 and 28 compare the water vapor barrier properties of the equivalent films. Figure 27 compares the WVTR while Figure 28 compares the WVPR. Generally, permeation rate, which is the transmission rate normalized to thickness, is not used for multilayer films, as it is not known what barrier is provided by what layer and at what thickness. Therefore, Figure 26 and Figure 28 are only provided for comparison purposes.

The multilayer control had greater oxygen barrier properties than the monolayer control. In Figure 25, the OTR of the monolayer microsphere-loaded films, unlike the monolayer control, were significantly less than the multilayer loaded films. However, as can be seen in Figure 26, the multilayer microsphere-loaded films, like the multilayer control, had an OPR less than the monolayer loaded films. This is because the multilayer films are approximately double the thickness of the monolayer films; therefore, on a per mil basis multilayer film processing does indeed improve the oxygen barrier properties. This improved barrier is only reflected in the OPR because it accounts for thickness while OTR does not.

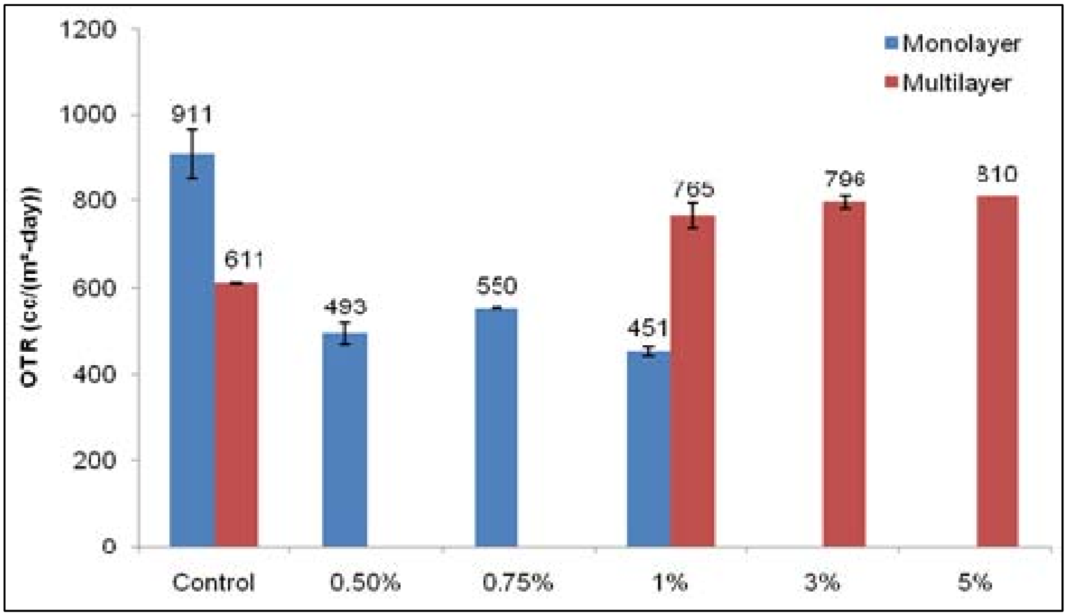


Figure 25: OTR of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE

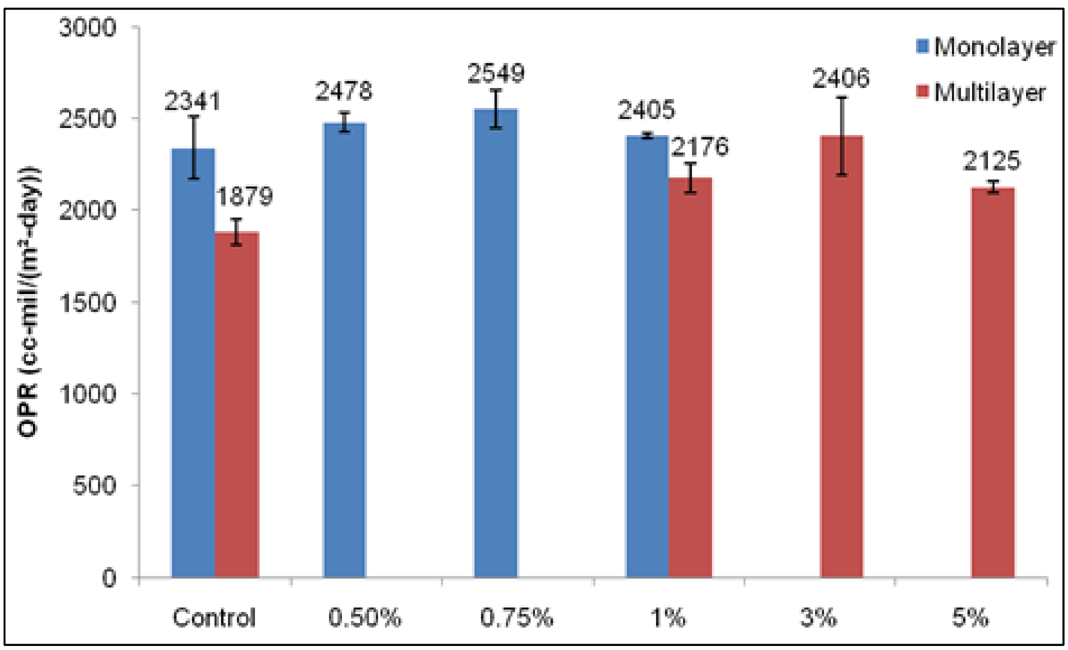


Figure 26: OPR of High Temperature Profile Monolayer and Multilayer Blown 930DU120 Microsphere-Loaded HDPE

As shown in both Figures 27 and 28, the WVTR and WVPR of the multilayer microsphere-loaded films were higher than the monolayer films. However, the multilayer control films were found to have greater water vapor barrier properties than the monolayer control films. The monolayer control had a WVTR of 1.331 g/m²-day while the multilayer control had a WVTR of only 1.086 g/m²-day. The difference between the WVPR of the two controls was much less, when taking the thickness of the films into account. The WVPR of both

the monolayer and multilayer films were found to increase with increasing microsphere loading levels, showing that multilayer film processing did not improve the water vapor barrier properties of the microsphere-loaded HDPE blown films.

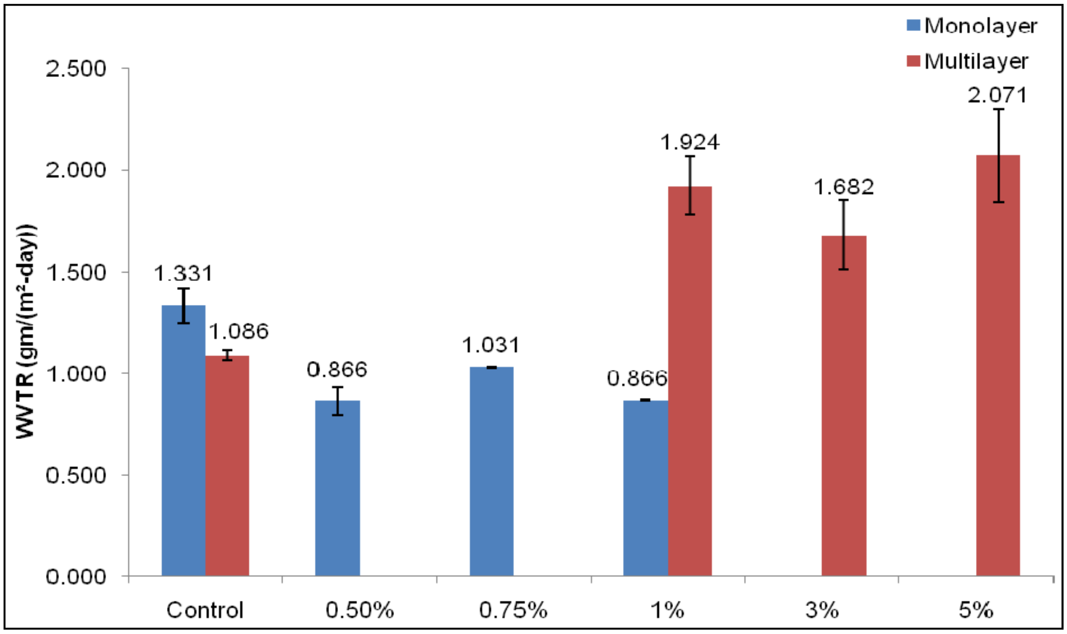


Figure 27: WVTR of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE

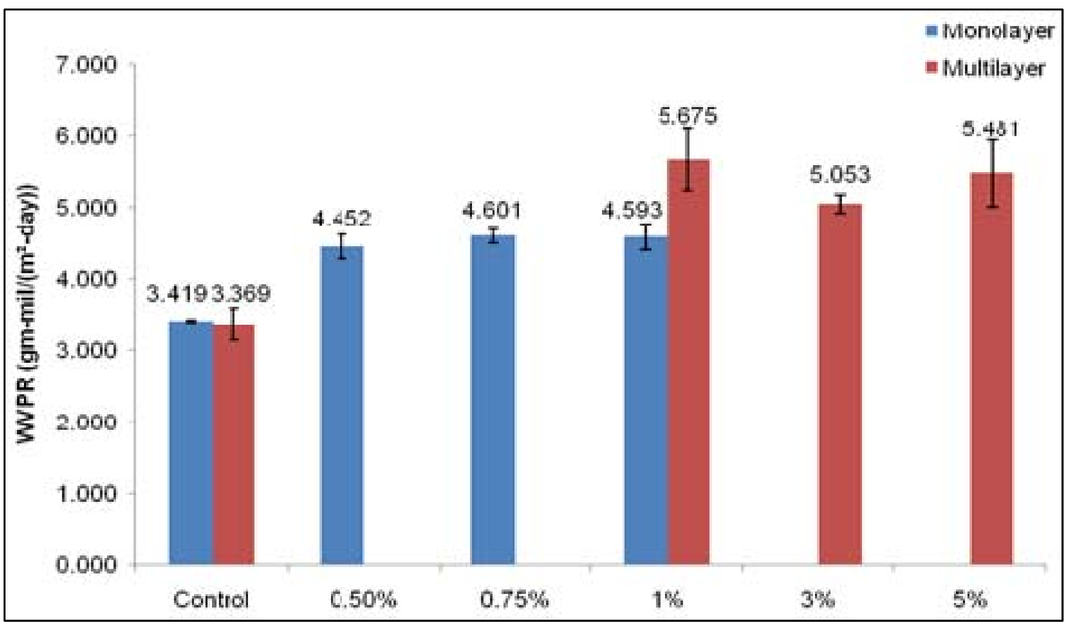


Figure 28: WVPR of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE

3.2.3 Density Measurement

Figure 29 shows the density of the control and 930DU120 microsphere-loaded HDPE blown films. As with the other measures, the density of the monolayer and multilayer control HDPE varied slightly, but were within standard deviation. The multilayer 1% microsphere-loaded HDPE had a density 8% higher than the monolayer 1% microsphere-loaded film. A slightly higher density was expected with processing of the multilayer film than the monolayer film, as co-extrusion introduces neat HDPE skin layers. However, the inclusion of neat skin layers was found to significantly reduce the surface texture created by the expansion of the microspheres and also increased melt strength so that higher microsphere loading levels could be processed. It should also be noted that, although the density of the monolayer 1% microsphere-loaded film was less than the multilayer 1% film as compared to the control, the addition of the microspheres still reduced the density of the HDPE film by approximately 24%.

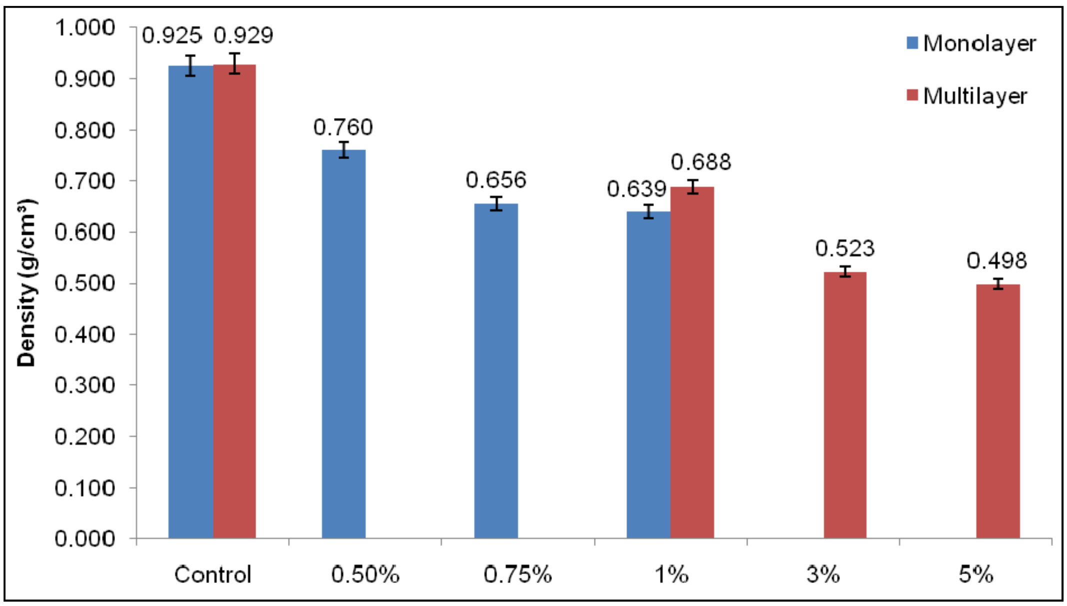


Figure 29: Density of High Temperature Profile Blown Monolayer and Multilayer 930DU120 Microsphere-Loaded HDPE

3.2.4 Thermal Analysis

The results of the thermal analysis of the multilayer control and 930DU120 microsphere-loaded HDPE blown films are shown in Figure 30. Both the thermal conductivity and thermal effusivity of the multilayer HDPE microsphere films decreased with increasing microsphere loading levels. A 60% decrease in thermal effusivity and an 80% decrease in thermal conductivity were observed at 1% microsphere loading. An additional 13% decrease in thermal effusivity and 28% decrease in thermal conductivity were observed between the 1% loading and the 5% loading. These decreases in thermal effusivity and conductivity correspond to an increase in insulation, indicating that polymeric microspheres provide thermal insulation.

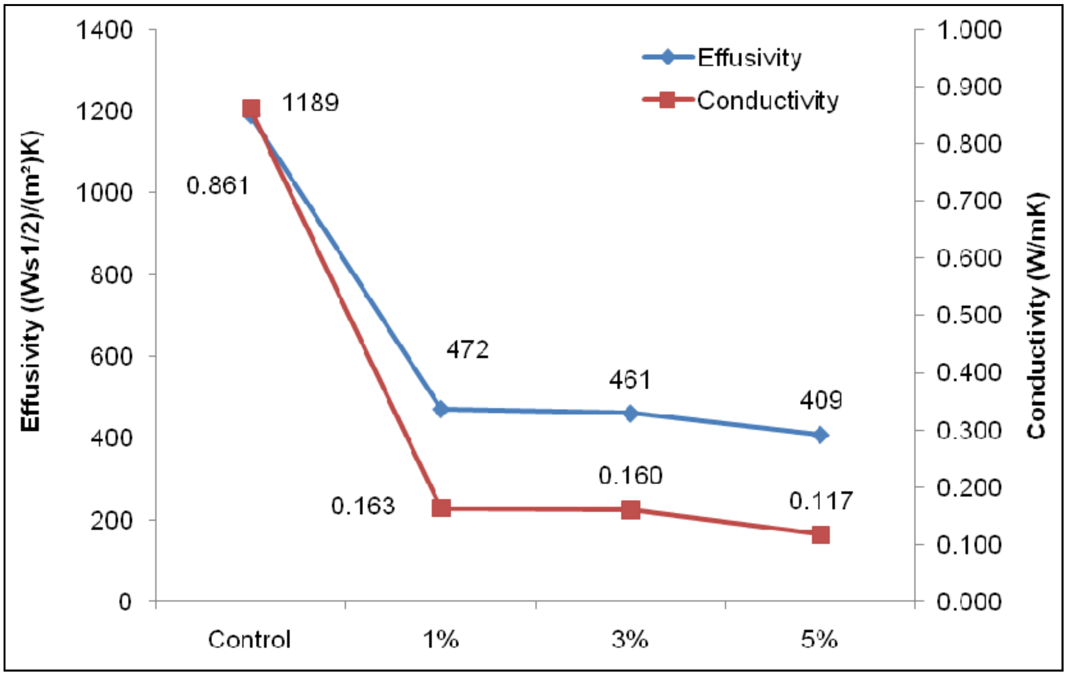


Figure 30: Thermal Analysis of High Temperature Profile Blown Multilayer 930DU120 Microsphere-Loaded HDPE

3.2.5 Discussion of Second Trial Results

The second processing trial determined that multilayer blown film processing produced a microsphere-loaded film with increased toughness, stress at yield, and strain at break; improved oxygen barrier properties; and reduced density. The multilayer film processing allowed for microsphere expansion and increased microsphere loading levels while maintaining a smooth surface texture and the melt strength necessary for blown film processing. It was also determined that the polymeric microspheres improved the thermal insulation of the polymer films, as decreases in thermal effusivity and thermal conductivity were observed. However, film processing with dry unexpanded microspheres required the additional step of milling the polymer pellets into a powder prior to processing in order to ensure sufficient blending of the polymer and microspheres.

3.3 Third Processing Trial

Because of the need to mill the polymer pellets into a powder prior to processing in the second trial, the third processing trial utilized a microsphere masterbatch (930MB120), which was a pelletized compound of 65% 930DU120 microspheres in an ethylene vinyl acetate matrix. This trial was designed to examine both HDPE and PP utilizing monolayer and multilayer, blown and cast film extrusion processing with microspheres loaded at various levels up to 9.75%. However, the 9.75% microsphere-loaded films lacked the melt strength necessary for blown and cast film extrusion processing. Melt strength decreased with increasing microsphere loading levels and became insufficient at levels greater than 5%. Therefore, film samples for

9.75% loading could not be obtained for testing and analysis. Each of these film combinations was processed at the high temperature profile with loading levels of 1.6%, 2.4%, and 3.3% of the microsphere masterbatch. These microsphere-loaded films and the corresponding controls were analyzed for mechanical properties and density during the third trial. In addition, the microsphere-loaded films were visually inspected for microsphere concentration, flexibility, and surface defects using optical microscopy. Barrier and thermal analyses were not completed on these films due to time and schedule constraints.

As mentioned in Section 2.2.3, monolayer film structure and cast processing were included in the design of the third trial, after not being tested in the second trial, in order to quantify the improvement in blown processing compared to cast and the improvement in multilayer compared to monolayer provided through use of the masterbatch. PP was processed and tested during this trial to apply the microsphere technology to another commonly used polymer, given the success of the HDPE processing during the second trial.

3.3.1 Mechanical Properties

Young's modulus and stress at yield, or tensile strength, were measured during the third trial. Figure 31 and Figure 32 compare measurements of those properties, respectively, of the monolayer and multilayer, blown and cast, and control and microsphere-loaded HDPE films. Figure 33 and Figure 34 compare the measurements of those properties, respectively, for the equivalent PP films. No trends were observed with the strain at break of the microsphere-loaded HDPE films with respect to increasing microsphere loading level.

As can be seen in Figure 31, the multilayer cast control had a Young's modulus 40% higher than the monolayer cast control, but the monolayer blown control had a Young's modulus 10% higher than the multilayer blown control. With one exception (3.3% multilayer blown), the microsphere-loaded films had higher Young's modulus values than the control HDPE films, indicating that addition of the microspheres improved the Young's modulus of the films. In general, the multilayer films had a higher Young's modulus than the monolayer films, except for the 1.6% cast and the 3.3% blown films, which had higher values for monolayer.

As can be seen in Figure 32, all of the blown microsphere-loaded HDPE films except one (the 1.6% multilayer, which was higher) had stress at yield values significantly less than the control HDPE. However, the standard deviation of the multilayer cast film samples was large, indicating inconsistencies in the film samples, as the values for the 1.6% and 2.4% samples were more than twice as high the multilayer cast control. It was noted during processing that the HDPE pellets did not feed consistently into the extruders, which could have caused inconsistencies in the HDPE films. Figure 32 also shows that all three monolayer microsphere-loaded cast HDPE films had stress at yield values higher than the cast control.

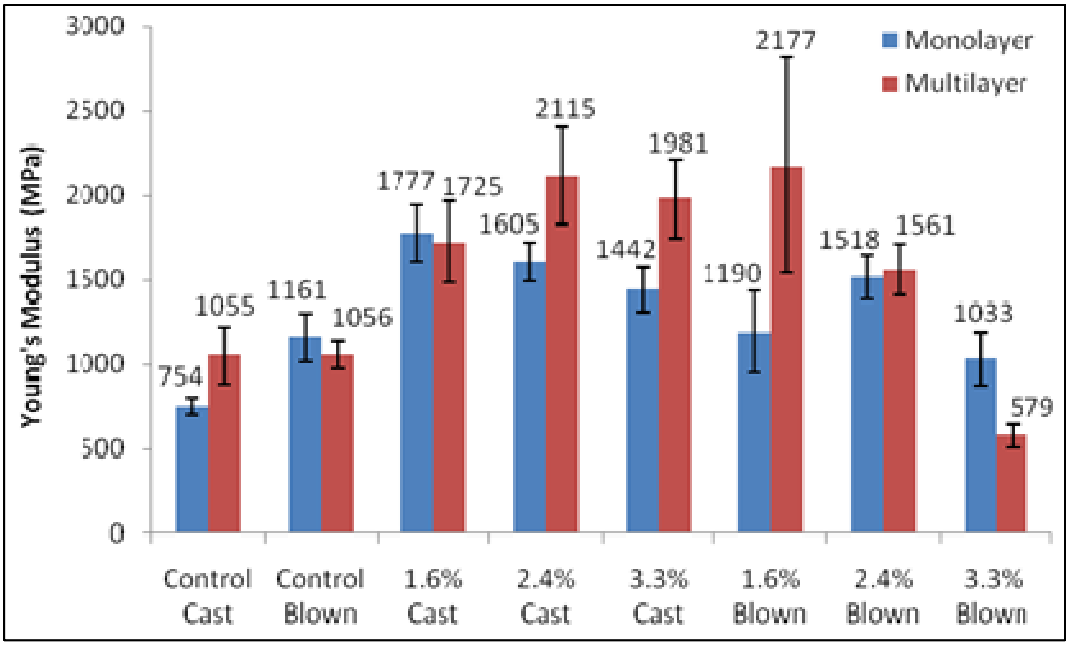


Figure 31: Young's Modulus of Masterbatch 930MB120 Microsphere-Loaded HDPE

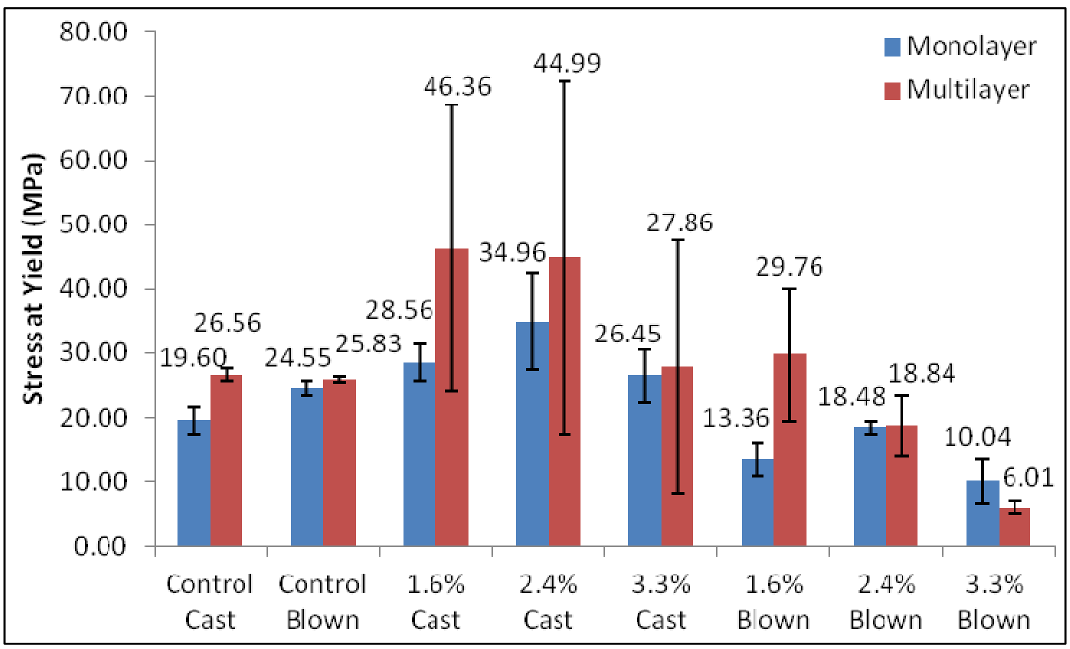


Figure 32: Stress at Yield of Masterbatch 930MB120 Microsphere-Loaded HDPE

As can be seen in Figure 33 and Figure 34, the addition of polymeric microspheres to the PP decreased Young's modulus and stress at yield for both the blown and cast films. In general, the multilayer microsphere-loaded films were found to have higher Young's modulus and stress at yield values than the monolayer films. Interestingly, the monolayer PP control films were found to have higher Young's modulus values than the multilayer control PP films. The cast control monolayer and multilayer films had Young's modulus values within standard deviation. However, the blown control monolayer film had a Young's modulus of 2959 MPa while the

multilayer film had a Young's modulus of only 1963 MPa. It was expected that the monolayer and multilayer cast films would have similar tensile properties, as multilayer processing utilizing the same polymer throughout the structure would yield essentially a monolayer film. In general the PP films were found to have decreasing Young's modulus and stress at yield values with increasing microsphere loading levels. This result was expected, as the microspheres introduce free volume, which is not expected to improve mechanical properties.

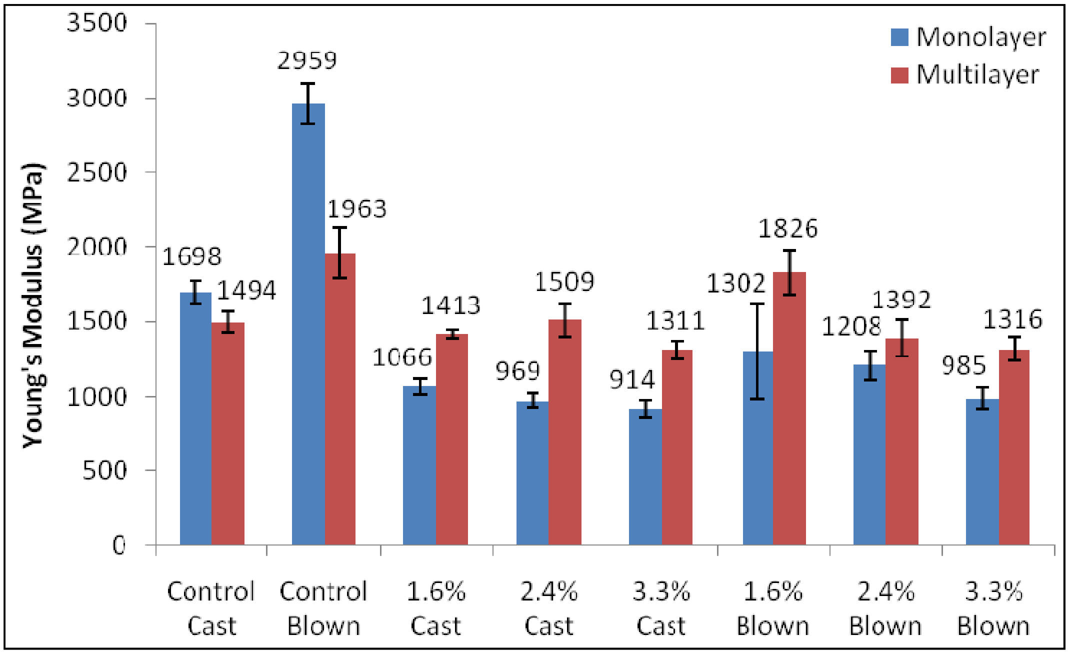


Figure 33: Young's modulus of Masterbatch 930MB120 Microsphere-Loaded PP

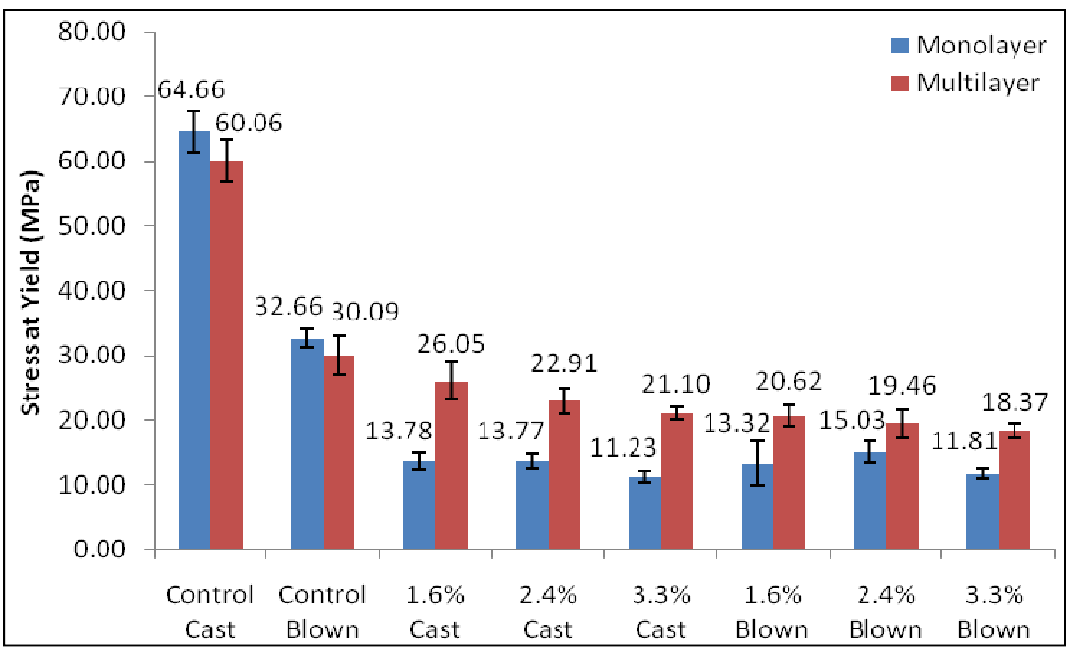


Figure 34: Stress at Yield of Masterbatch 930MB120 Microsphere-Loaded PP

3.3.2 Density Measurement

Figure 35 compares the density of monolayer and multilayer, blown and cast, and control and microsphere-loaded HDPE films. As can be seen in Figure 35, the microsphere-loaded monolayer and multilayer HDPE density values were similar to each other in each of the cast films and in the control and 2.4% blown films, while the 1.6% and 3.3% monolayer blown films showed much lower density than the multilayer films. It is possible that the 2.4% blown HDPE film samples were collected before the process reached steady state conditions, as the density of the monolayer and multilayer samples were almost the same. The monolayer 2.4% blown HDPE film had a density of 0.653 g/cm³ while the multilayer 2.4% blown HDPE film had a density of 0.650 g/cm³. There was no change in density with the cast film processing of the monolayer and multilayer HDPE films; however, there was a significant decrease in density with blown film processing of both the monolayer and multilayer films.

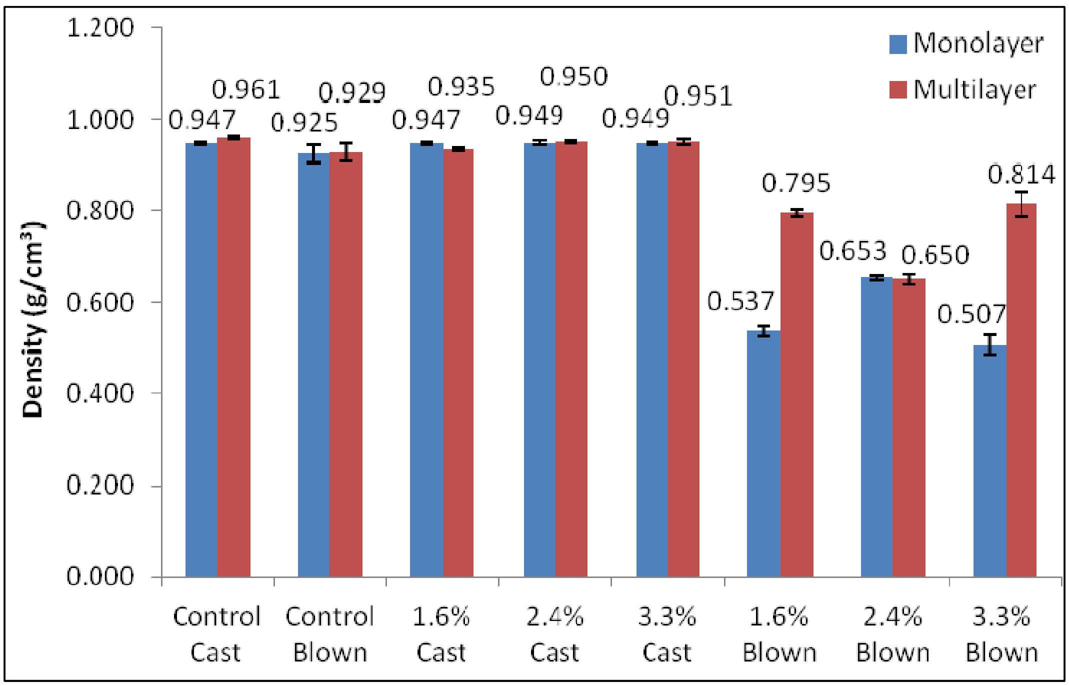


Figure 35: Density of Masterbatch 930MB120 Microsphere-Loaded HDPE

Figure 36 compares the density of monolayer and multilayer, blown and cast, and control and microsphere-loaded PP film. It shows that the densities of the monolayer blown and cast PP films were significantly less than the multilayer films at all microsphere loading levels. In addition, Figure 36 shows that the blown microsphere-loaded films had lower densities than the cast films while the blown and cast controls were nearly the same at each structure, showing that the blown film process allowed for increased microsphere expansion in both the monolayer and multilayer systems, as previously discussed. The monolayer films should have a density less than the multilayer films, as the multilayer films incorporate neat polymer skin layers which increase density of the polymer film produced.

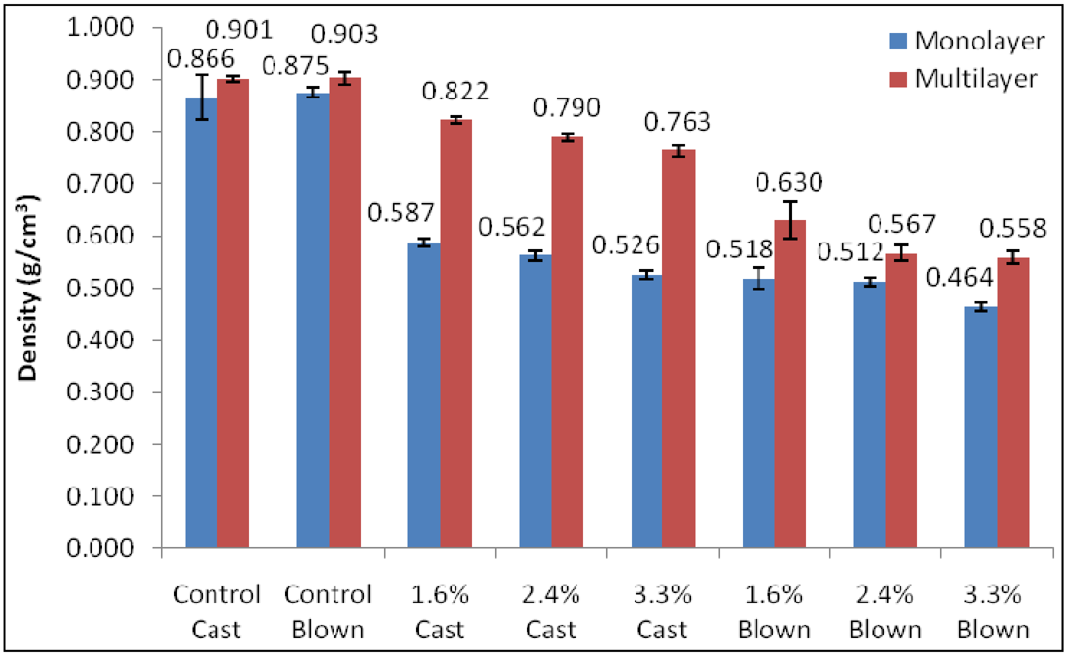


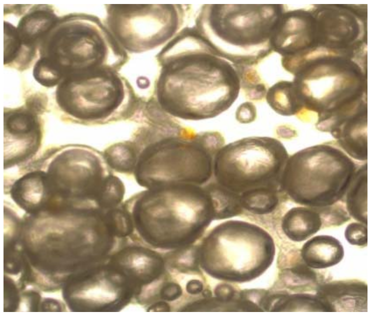
Figure 36: Density of Masterbatch 930MB120 Microsphere-Loaded PP

3.3.3 Optical Microscopy

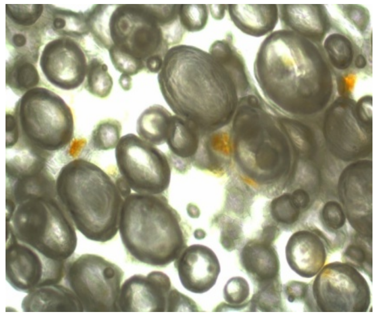
Optical microscopy was not completed on the HDPE films because of the inconsistencies observed in the tensile and density analyses. Figure 37 shows the optical microscopy images of the microsphere-loaded monolayer blown and cast PP films, and Figure 38 shows the optical microscopy images of the microsphere-loaded multilayer blown and cast PP films. The monolayer films (shown in Figure 37) had a higher microsphere concentration than the multilayer films (shown in Figure 38), possibly due to the thickness of the films. The monolayer films were thicker than the microsphere-loaded cores in the multilayer films.

Figure 37 shows a greater microsphere expansion in the blown films than in the cast films. It was expected that the blown films would exhibit increased microsphere expansion, as the blown film process allows for increased microsphere expansion time before solidification of the polymer melt.

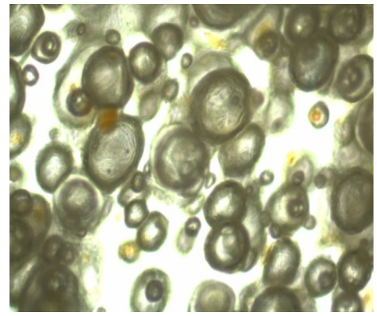
Figure 38 shows a higher microsphere concentration and smaller microsphere size in the cast films than in the blown films. The cast films were found to be approximately double the thickness of the blown films, indicating that a greater concentration of microspheres would be observed. This processing trial determined that microsphere-loaded PP films displayed the same reduction in mechanical properties and density as observed with the microsphere-loaded HDPE films, indicating that microspheres could be successfully compounded into various polymer matrices in order to produce films with decreased weight and density.



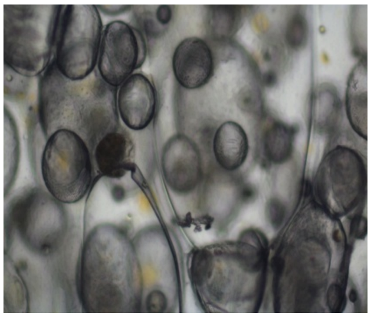
a: 1.6% Cast PP



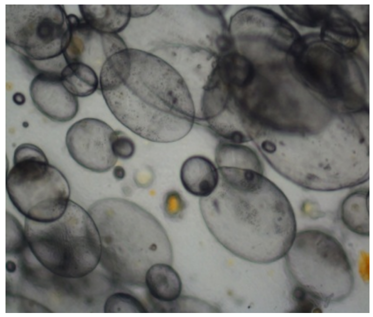
b: 2.4% Cast PP



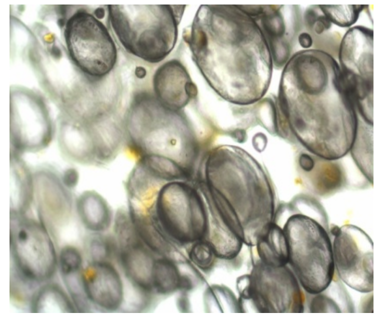
c: 3.3% Cast PP



d: 1.6% Blown PP

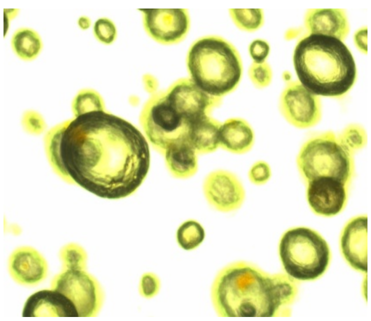


e: 2.4% Blown PP

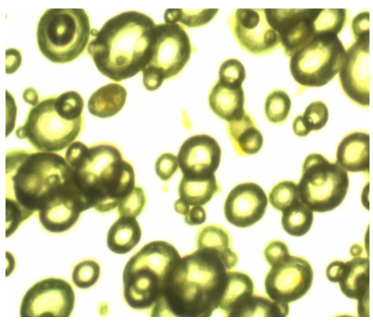


f: 3.3% Blown PP

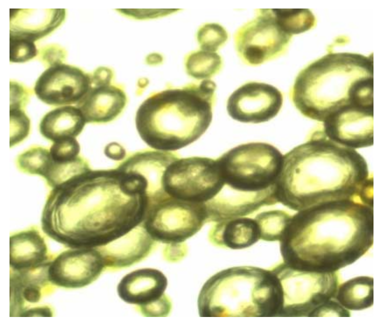
Figure 37: Optical Microscopy of Monolayer Masterbatch 930MB120 Microsphere-Loaded PP



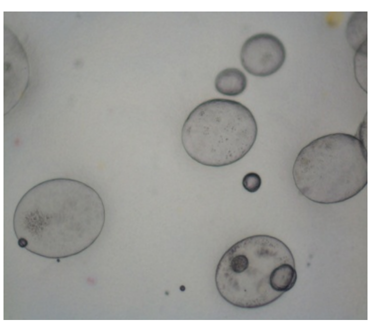
a: 1.6% Cast PP



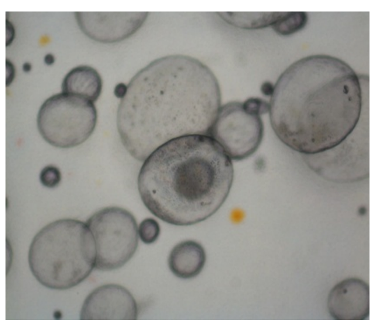
b: 2.4% Cast PP



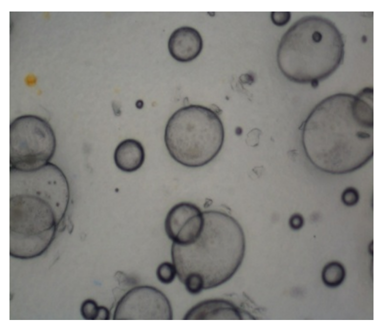
c: 3.3% Cast PP



d: 1.6% Blown PP



e: 2.4% Blown PP



f: 3.3% Blown PP

Figure 38: Optical Microscopy of Multilayer Masterbatch 930MB120 Microsphere-Loaded PP

3.3.4 Discussion of Third Trial Results

The results from the third processing trial show that microsphere-loaded films can be successfully processed at loading levels below 5%. Similar trends were observed with both HDPE and PP, indicating that microspheres can be successfully processed in a variety of polyolefin-based polymer matrices. Attempts to achieve microsphere loading levels of 9.75% for use in the third trial produced a film that lacked the melt strength necessary for cast or blown film extrusion processing at levels greater than 5%. The third trial also confirmed that blown multilayer processing produced films with the best balance of properties as compared to monolayer structure or cast processing.

In addition, the Flint Hills Resources H3108 HDPE exhibited surging in the extruders during processing in the third trial. Surging is a variation in the output of an extruder and is a common extrusion problem that can be caused by many sources including resin feedstock and screw geometry [10]. Improper solids conveying and melting instabilities can be mitigated through modification of the extruder screw design or altering of the resin feedstock.

4. Conclusions and Future Work

The objective of this research was to extrude process films with optimal microsphere loading levels in order to reduce the weight and improve the mechanical, barrier, and thermal properties of ration packaging materials. This study determined that a polyolefin film with microsphere loading up to 5% could successfully be processed utilizing conventional extrusion equipment. PP and HDPE were investigated in this study, and both were found to exhibit a decrease in mechanical properties, barrier properties, density, thermal effusivity, and conductivity.

It was found that the significant reduction in density provided by the introduction of free volume into the polyolefin films through the use of microspheres (1) would allow for lighter military ration packaging, (2) would reduce cost through the use of less resin to produce the same thickness polymer film, and (3) could improve thermal insulation for the FRH pouch and, in turn, faster heating of the Warfighter's entrée through increased heating efficiency. The FRH, which is provided in every MRE™, consists of a magnesium iron compound heater in a disposable monolayer HDPE pouch. The MRE™ entrée is inserted into the pouch with the water activated FRH, which heats the entrée to serving temperature. In addition to the FRH pouch, another possible application for use of polymeric microspheres is the MRE™ menu bag.

The investigation of polymeric microspheres for food packaging applications will continue as a CFREP joint statement need (JSN) project entitled *Packaging Optimization with Polymeric Microspheres*. This project is funded for three years, FY11 through FY13. It focuses on applied research and advanced technology development. The purpose of that project is to provide information on the development of polymeric films containing expandable microspheres to improve performance, reduce costs, and reduce density of military food packaging. Objectives include (1) the reduction of density and improvement of thermal insulation properties through the optimization of microsphere-loaded multilayer co-extruded or laminated films and (2) the development of a polymeric microsphere-loaded thermoplastic film for use in military food packaging applications, specifically the FRH pouch and the MRE™ menu bag.

Based on the three trials, the blown multilayer film loaded with masterbatch 930MB120 microspheres produced at the high temperature using either HDPE or PP is recommended for use in future processing and analysis, as this combination with HDPE or PP was shown to be the produce film with greatest viability and most beneficial properties using either polymer. However, Flint Hills Resources H3108 HDPE is not recommended for use in subsequent processing trials, as changing the resin feedstock rather than modifying the screw is more easily accomplished to address the surging in the extruders that was exhibited during processing in the third trial.

Blown film extrusion produced microsphere-loaded films with greater microsphere expansion and more even dispersion than cast film extrusion. Blown film processing allowed additional time for the polymer matrix to cool, thereby increasing microsphere expansion in the

polymer film. Multilayer film extrusion provided greater melt strength than the monolayer film to enable processing of increased microsphere loading levels. Multilayer blown film processing was found to increase the mechanical properties and also slightly increase the density of the HDPE or PP films produced. The high temperature profile produced films that were more flexible and had a greater and more uniform microsphere concentration, fewer surface defects, and greater decreased tensile and barrier properties than the films produced at the low temperature profile. .

This document reports research undertaken at the U.S. Army Natick Soldier Research, Development and Engineering Center, Natick, MA, and has been assigned No. NATICK/TR- 12/020 in a series of reports approved for publication.

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